## HANCOKINOL, A NOVEL TRITERPENE, FROM CYNANCHUM HANCOKIANUM

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Summary: Absolute stereochemistry of hancokinol, a novel triterpene, isolated from *Cynanchum hancokianum*, has been elucidated by means of spectroscopic and X-ray analyses.

Cynanchum hancokianum (Maxim.) Al. Iljinski. (Asclepiadaceae), distributed in Inner Mongolia, is known as a Chinese folk medicine possessing antitumor activity. Our investigations have led to the isolation of two phenanthroindolizine alkaloids from the hydrochloric acid extract.<sup>1</sup> We now report the structural elucidation of a new pentacyclic triterpene, named hancokinol, isolated from the ethanol extract of the same plant source by means of spectroscopic and X-ray analyses.

Hancokinol (1),  $C_{30}H_{50}O$ ,<sup>2</sup> was obtained as colorless needles, mp 229–230° (MeOH),  $[\alpha]_D^{20}$  +16.2° (c=0.77, CHCl<sub>3</sub>), +16.6° (c=0.49, dioxane), IR (CHCl<sub>3</sub>) 3580 cm<sup>-1</sup> (OH).

Protons and carbons were assigned by 2D NMR spectroscopy (Table 1).<sup>3</sup> DEPT experiments showed the presence of eight methyls, nine methylenes. seven methines and six quaternary carbons. <sup>1</sup>H-<sup>1</sup>H COSY experiments showed the presence of an *i*-propyl comprised of two s-methyls at  $\delta_{\rm H}$  0.87 (H<sub>3</sub>-29) and 0.90 (H<sub>3</sub>-30) and a methine at  $\delta_{\rm H}$  1.57 (H-20). A methine at  $\delta_{\rm H}$  1.57 (H-19) was correlated to a methine at  $\delta_{\rm H}$  1.48 (H-18) and H-20, leading to  $Pr^{i}$ -19. A one-proton signal at  $\delta_{\rm H}$  5.54 was attributed to a trisubstituted olefinic proton (H-6) possessing a neighboring methylene at  $\delta_{\rm H}$  2.26, 2.01 (H<sub>2</sub>-7). <sup>1</sup>H-<sup>1</sup>H and <sup>1</sup>H-<sup>13</sup>C COSY experiments placed a hydroxymethine ( $\delta_{\rm H}$  3.47,  $\delta_{\rm C}$  76.58, C-3) between a methylene ( $\delta_{\rm H}$  1.90, 1.69,  $\delta_{\rm C}$  28.81, C-2) and a quaternary carbon ( $\delta_{\rm C}$  41.32, C-4) containing two gem-methyls ( $\delta_{\rm H}$  1.04,  $\delta_{\rm C}$  27.26, C-23)( $\delta_{\rm H}$  1.13,  $\delta_{\rm C}$  25.39, C-24). The hydroxyl was assigned to be axial on the basis of coupling (t, J=2.5 Hz) observed for the methine proton. The correlations of two methines at  $\delta_{\rm H}$  1.48 (H-8) and 2.35 (H-10) to neighboring methylenes at  $\delta_{\rm H}$  2.26 (H $\beta$ -7)

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No $o_{C}$ $o_{H}$ with $C^{-}$ with $H^{-2}$ with $H^{-2}$ 1 20.80 t $Ha^{-1}$ 1.42 m $Ha,\beta^{-2}, H^{-3}, H^{-10}$ $Ha^{-1}, Ha^{\beta}_{-2}, H^{-10}$ $Ha^{-1}$ 1.59 m $Ha^{-2}$ 1.69 m $Ha^{-1}, Ha^{-2}, H^{-3}$ (2.5, 4.0, 14.0) $Ha^{-2}$ 1.69 m $Ha,\beta^{-1}, Ha^{-2}, H^{-3}$ (2.5) $Ha^{-2}$ 1.69 m $Ha,\beta^{-1}, Ha^{-2}, H^{-3}$ 4 41.32 s (2.5) $Ha^{-2}, H_3^{-23}, H_3^{-24}$ 6 121.47 d $H^{-6}$ 5.54 dt $Ha,\beta^{-7}, H^{-8}$ $Ha,\beta^{-7}$ (19.0, 6.0) $H\beta^{-7}$ 2.26 ddd $H^{-8}$ $H^{-6}, Ha^{-7}, H^{-8}$ (19.0, 6.0) $H\beta^{-7}, H_3^{-25}, H_3^{-26}$ $Ha^{-7}$ 1 30.64 t $H_{-11}$ 1.13 m $H^{-8}, H_3^{-25}$ $Ha,\beta^{-12}$ 1 30.64 t $H_{-11}$ 1.159 m $H\beta^{-12}, H^{-26}, H_3^{-26}$ $Ha,\beta^{-12}$ 1 30.64 t $H_{2^{-11}}$ 1.13 m $H^{-8}, H_3^{-25}$ $Ha,\beta^{-12}$ 1 39.25 s $Ha^{-7}, H^{-8}, H_3^{-26}, H_3^{-26}$ $Ha^{-7}, Ha^{-12}, Ha^{-12}$ 1 4 39.62 s $Ha^{-12}, 1.25$ m $Ha^{-22}, H^{-28}, Ha^{-12}$ 1 5 29.38 t $H_{2^{-15}}$ 1.25 m $Ha^{-22}, H^{-28}, Ha^{-28}$ $Ha^{-16}, Ha^{-12}, Ha^{-22}$ 1 7 39.92 s $Ha^{-27}, Ha^{-28}, Ha^{-28}, Ha^{-16}, Ha^{-29}$ $Ha^{-18}, Ha^{-18}, Ha^{-28}, Ha^{-28}$ $Ha^{-18}, Ha^{-18}, Ha^{-28}, Ha^{-28}$ 1 4 4 2.4 d $H^{-18}$ 1.48 m $H^{-18}, H_3^{-26}, H_3^{-26}$ $H_2^{-16}, Ha^{-28}, Ha^{-28}$ 1 4 $Ha^{-22}, Ha^{-28}, Ha^{-28}, Ha^{-28}, Ha^{-28}, Ha^{-18}, Ha^{-18}, Ha^{-18}, Ha^{-18}, Ha^{-28}, Ha^{-18}, Ha^{-18}, Ha^{-18}, Ha^{-18}, Ha^{-18}, Ha^{-18}, Ha^{-18}, Ha^{-18}, Ha^{-28}, Ha^{-18}, Ha^{-28}, Ha^{-28}, Ha^{-30}$ 1 9 48.24 d $H^{-18}$ 1.49 m $H^{-28}, Ha^{-28}, Ha^{-30}, Ha^{-28}, Ha^{-30}$ 1 9 48.24 d $H^{-18}$ 1.48 d $Ha^{-12}, Ha^{-28}, Ha^{-30}, Ha^{-28}, Ha^{-21}, Ha^{-28}, H$		Carbon		Correlated H <sup>D</sup>	H coupled	H coupled
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	NO	δC		0 H		with H <sup>*</sup>
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1	20.80	t	H <b>α</b> -1 1.42 m Hβ-1 1.59 m	H <b>α,β</b> −2, H−3, H−10	Нβ−1, Нβ−2, Н−10 Нα−1, На,β −2, Н−10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	28.81	t	Hα-2 1.90 ddt (2.5, 4.0, 14.0)		Hβ−1, Hβ−2, H−3
3 76.58 d H-3 3.47 t $H\rho-1, H_3-23$ $H\alpha, \beta-2$ 4 41.32 s (2.5) 4 41.32 s (2.5) 6 121.47 d H-6 5.54 dt Ha, $\beta-7$ (2.6) 4 $Ha-7$ 2.01 dd H-8 Ha, $\beta-7$ (19.0, 6.0) Ha-7 2.26 ddd H-6, $Ha-7$ , H-8 Ha, $\beta-7$ (19.0, 6.0) Ha-7 2.26 ddd H-8, $H_2-11, H_3-25$ Ha, $\beta-1$ (12.0) 1 37.23 d H-10 2.35 d H-8, $H_3-25$ Ha, $\beta-1$ (12.0) 1 30.64 t $H_{2-111}$ 1.13 m H-8, $H_3-25$ Ha, $\beta-1$ (12.0) 1 30.64 t $H_{2-111}$ 1.13 m H-8, $H_3-25$ Ha, $\beta-1$ (12.0) 1 30.64 t $H_{2-111}$ 1.30 m H-8, $H_3-25$ Ha, $\beta-1$ (12.0) 1 4 39.62 s Ha-12 1.36 m Ha-2, $H_3-26$ H $\beta-7$ 1 4 39.62 s Ha-16 1.49 m H $\beta-22, H_3-26$ H $2-11, Ha-12$ 1 5 29.38 t $H_{2-15}$ 1.25 m H-8, $H_2-16, H_3-26$ H $2-16$ H $2-16$ 1 $H_2-12, H_3-27$ H $\beta-7$ , H-8, $H-18, H_3-26$ H $2-16$ H $2-16$ 1 $H_2-12, H_3-28$ H $2-15, H_3-27$ H $\beta-2, H_3-28$ H $2-15$ 1 $H_2-12, H_3-28$ H $2-15, H_3-27$ H $\beta-2, H_3-28$ H $2-15$ H $2-21, Ha-22, H-19$ 1 $H_2-12, H_3-28$ H $2-15, H_3-28$ H $2-15$ H $2-21, Ha-22, H-19$ H $2-12, Ha-22, H-19$ H $2-21, Ha-22, H-21, Ha-22, Ha-21, Ha-22, Ha-23, Ha-23, Ha-23, Ha-23, Ha-21, Ha-22, Ha-24, Ha-23, Ha-23, Ha-23, Ha-21, Ha-22, Ha-24, Ha-23, Ha-23, Ha-24, Ha-23, Ha-24, Ha$				H <b>β</b> −2 1.69 m		Н <b>а, β-</b> 1, Н <b>а</b> -2, Н-3
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3	76.58	d	H-3 3.47 t (2.5)	Hβ-1, H <sub>3</sub> -23	H <b>α, β</b> -2
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4	41.32	S		H <b>β</b> -2, H <sub>3</sub> -23, H <sub>3</sub> -24	
6 121. 47 d H-6 5. 54 dt Ha, $\beta$ -7, H-8 Ha, $\beta$ -7, H-8 Ha, $\beta$ -7, H-8 Ha, $\beta$ -7 (6. 0, 2. 0) 7 22. 65 t Ha -7 2. 01 dd H-8 H-6, H $\beta$ -7 9 32. 49 s H-7 2. 26 ddd H-8 H $\beta$ -7, H <sub>3</sub> -25, H <sub>3</sub> -26 H $\beta$ -7 9 34. 49 s H-8 1. 48 m H $\beta$ -7, H <sub>3</sub> -25, H <sub>3</sub> -26 H $\beta$ -7 9 34. 49 s H-10 2. 35 d H-8, H <sub>3</sub> -25 Ha, $\beta$ -1 11 30. 64 t H <sub>2</sub> -11 1. 13 m H-8, H <sub>3</sub> -25 Ha, $\beta$ -1 12 30. 72 t Ha -12 1. 59 m H_{2} -11, H $\alpha$ -12, H=18 H $\beta$ -7 13 39. 25 s H-8, H_2 -11, H $\alpha$ -12, H=18, H <sub>3</sub> -26, H <sub>3</sub> -27 14 39. 62 s H $\beta$ -7 15 29. 38 t H <sub>2</sub> -15 1. 25 m H-8, H <sub>2</sub> -16, H <sub>3</sub> -26 H <sub>2</sub> -16 16 32. 65 t H <sub>2</sub> -16 1. 49 m H $\beta$ -22, H <sub>3</sub> -28 H <sub>1</sub> -18, H-21, H $\alpha$ -12 17 39. 92 s H <sub>2</sub> -16 1. 49 m H $\beta$ -22, H <sub>3</sub> -28 H-18, H-18, H-20, Ha -21 19 48. 24 d H-19 1. 57 m Hb -21, H $\alpha$ -22, H-19 19 48. 24 d H-19 1. 57 m Hb -21, H $\alpha$ -22, H-19 19 48. 24 d H-19 1. 57 m Hb -21, H $\alpha$ -22, H-19, H <sub>3</sub> -30 11 27. 85 t Ha -21 1. 44 m H-18, H <sub>3</sub> -28 Ha -20, Ha -30 11 4 $\beta$ -22 1. 79 dd Ha -21, H $\beta$ -22 12 37. 85 d Ha -20, 1. 49 m H-18, H <sub>3</sub> -28 Ha -21, H $\beta$ -22 14 $\beta$ -22 1. 79 dd Ha -22, Ha -30 15 29. 38 d H -20 1. 49 m H-18, H <sub>3</sub> -28 Ha -30 16 32. 66 d H-20 1. 49 m H-18, H <sub>3</sub> -28, H <sub>3</sub> -30 17 39. 92 s Ha -30 Ha -21, H $\alpha$ -22, H-19 18 48. 24 d H -19 1. 57 m Ha -21, H $\alpha$ -22, H-19 19 48. 24 d H -19 1. 57 m Ha -21, H $\alpha$ -22, H-19, Ha -21, H $\alpha$ -22 16 1. 67 m Ha -21, 1. 67 m 17 39. 92 s Ha -30 Ha -20, H $\beta$ -22 18 5. 46 d H-20 1. 49 m H-18, H <sub>3</sub> -28 Ha -30 19 48. 24 4 H $\alpha$ -22 1. 27 m Ha -18, H <sub>3</sub> -28 Ha -20, H $\beta$ -22 19 4. 2. 44 t H $\alpha$ -22 1. 27 m Ha -28 Ha -20, H $\beta$ -22 10 37. 26 q H <sub>3</sub> -26 0. 80 s Ha -21, H $\alpha$ -22 13 27. 26 q H <sub>3</sub> -28 0. 93 s H <sub>3</sub> -24 24 25. 39 q H <sub>3</sub> -26 0. 80 s Ha -24 25 28. 77 q H <sub>3</sub> -26 0. 80 s Ha -24 26 15. 39 q H <sub>3</sub> -26 0. 80 s Ha -26 17 16. 78 q H <sub>3</sub> -26 0. 80 s Ha -26 18 -20, Ha -20 19 2. 32. 44 q H <sub>3</sub> -30 0. 90 d H <sub>3</sub> -29 H-20 10 3. 90 d H <sub>3</sub> -29 Ha -20 10 4. 90 0. 90 d H <sub>3</sub> -29 Ha -20 10 4. 90 0. 90 d H <sub>3</sub> -29 Ha -20 10 4. 90 0. 90 d H <sub>3</sub> -29 Ha -20 10 4. 90 0. 90 d H <sub>3</sub> -29 Ha -20	5	140.64	S		$H_3 - 23, H_3 - 24$	
7 22.65 t $Ha-7$ 2.01 dd $H-8$ $H-6$ , $H\beta-7$ (19.0, 6.0) $H\beta-7$ 2.26 ddd $H-6$ , $Ha-7$ , $H-8$ (19.0, 3.2, 2.0) 8 44.54 d $H-8$ 1.48 m $H\beta-7$ , $H_3-25$ , $H_3-26$ H-6, $Ha-7$ , $H-89 34.49 s10 37.23 d H-10 2.35 d H-8, H_2-11, H_3-25 Ha,\beta-1(12.0)11 30.64 t H_2-11 1.13 m H-8, H_3-25 Ha,\beta-1(12.0)11 30.64 t H_2-11 1.13 m H-8, H_3-25 Ha,\beta-1Ha-12 1.59 m H_2-11, Ha-12Ha-12 1.59 m Ha-12, H_2-11, Ha-12H_2-11, Ha-1213 39.25 s Ha,\beta-12 Ha-12, Ha-22, Ha-18, Ha-20, Ha-3019 48.24 d H-19 1.57 m Ha-18, Ha-29, Ha-3020 35.96 d H-20 1.49 m H-18, Ha-29, Ha-3021 27.85 t Ha-21 1.44 m H-18, Ha-29, Ha-3021 27.85 t Ha-21 1.49 m H-18, Ha-29, Ha-3022 42.44 t Ha-22 1.25 m Ha-18, Ha-22, Ha-21, Ha-22, Ha-2$	6	121.47	d	H-6 5.54 dt (6.0, 2.0)	Hα,β-7, H-8	H <b>α, β</b> – 7
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	7	22.65	t	H <b>a</b> -7 2.01 dd	H-8	H-6, H <b>β-</b> 7
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				(19.0, 6.0)		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				H <b>β−</b> 7 2.26 ddd		H-6, H <b>a-</b> 7, H-8
8 44.54 d H-8 1.48 m $H\beta^{-7}$ , H <sub>3</sub> -25, H <sub>3</sub> -26 $H\beta^{-7}$ 9 34.49 s 10 37.23 d H-10 2.35 d H-8, H <sub>2</sub> -11, H <sub>3</sub> -25 $H\alpha,\beta-1$ (12.0) 11 30.64 t H <sub>2</sub> -11 1.13 m H-8, H <sub>3</sub> -25 $H\alpha,\beta-1$ 12 30.72 t H\alpha-12 1.59 m $H^{-12}$ 1.36 m $H^{-12}$ H <sub>2</sub> -11, H\alpha-12 H <sub>2</sub> -12 H <sub>2</sub> -16, H <sub>2</sub> -16 H <sub>2</sub> -16 H <sub>3</sub> -26 H <sub>3</sub> -27 H <sub>3</sub> -28 H <sub>2</sub> -16, H <sub>2</sub> -16, H <sub>2</sub> -16 H <sub>3</sub> -22, H <sub>3</sub> -28 H <sub>2</sub> -15 H <sub>2</sub> -16, H\alpha-22 H <sub>3</sub> -28 H <sub>2</sub> -15 H <sub>3</sub> -20, H <sub>3</sub> -20, H <sub>3</sub> -30 H <sub>3</sub> -29, H <sub>3</sub> -30 H <sub>3</sub> -22, H <sub>2</sub> -12, H\alpha-22 H <sub>2</sub> -12, H <sub>2</sub> -22 H <sub>2</sub> -12, H <sub>2</sub> -22 H <sub>2</sub> -12, H <sub>3</sub> -23 H <sub>3</sub> -30 H <sub>3</sub> -24 H <sub>3</sub> -23, H <sub>3</sub> -23 H <sub>3</sub> -30 H <sub>3</sub> -24 H <sub>3</sub> -21, H\alpha-22 H <sub>3</sub> -23 H <sub>3</sub> -30 H <sub>3</sub> -24 H <sub>3</sub> -23, H <sub>3</sub> -23 H <sub>3</sub> -30 H <sub>3</sub> -24 H <sub>3</sub> -23, H <sub>3</sub> -24 H <sub>3</sub> -24 H <sub>3</sub> -24 H <sub>3</sub> -24 H <sub>3</sub> -26 0.80 s H <sub>3</sub> -24 H <sub>3</sub> -21, H\alpha-22 H <sub>3</sub> -23 H <sub>3</sub> -30 H <sub>3</sub> -24 H <sub>3</sub> -23 H <sub>3</sub> -30 H <sub>3</sub> -24 H <sub>3</sub> -23 H <sub>3</sub> -30 H <sub>3</sub> -24 H <sub>3</sub> -23 H <sub>3</sub> -30 H <sub>3</sub> -24 H <sub>3</sub> -23 H <sub>3</sub> -30 H <sub>3</sub> -24 H <sub>3</sub> -23 H <sub>3</sub> -30 H <sub>3</sub> -24 H <sub>3</sub> -23 H <sub>3</sub> -30 H <sub>3</sub> -24 H <sub>3</sub> -23 H <sub>3</sub> -30 H <sub>3</sub> -24 H <sub>3</sub> -24 H <sub>3</sub> -24 H <sub>3</sub> -24 H <sub>3</sub> -26 0.80 s H <sub>3</sub> -24 H <sub>3</sub> -30 H <sub>3</sub>				(19.0, 3.2, 2.0)		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8	44.54	d	H-8 1.48 m	H <b>β-7,</b> H <sub>3</sub> -25, H <sub>3</sub> -26	H <b>β</b> −7
10 37. 23 d H=10 2. 35 d (12.0) 11 30. 64 t H_2=11 1. 13 m H=8, H_3=25 Ha, $\beta = 1$ 12 30. 72 t Ha=12 1. 59 m H=8, H_3=25 Ha=12 Ha	9	34.49	S		H-8, H <sub>2</sub> -11, H <sub>3</sub> -25	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10	37.23	d	H-10 2.35 d	H-8, H <sub>3</sub> -25	H <b>α,β</b> –1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	11	30 64	+	$H_{n} = 11 \ 1 \ 13 \ m$	H-8 Ha-25	$H\alpha \beta = 12$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	12	30 72	+	$H_{\alpha} = 12 \ 1 \ 50 \ m$	11 0, 113 20	$H_{0} = 11$ $H_{0} = 12$
13 39.25 s 14 39.62 s 14 39.62 s 14 39.62 s 15 29.38 t $H_{2}-15$ 1.25 m 17 39.92 s 18 54.46 d $H-18$ 1.48 d $Ha-12$ , $Ha-22$ , $H-18$ , $H_{3}-26$ $H_{2}-16$ 19 48.24 d $H-19$ 1.57 m H=0.21, $Ha-22$ , $H_{3}-28$ 10 35.96 d $H-20$ 1.49 m H=0.21, $Ha-22$ , $Ha-23$ , $Ha-21$ , $Ha-22$ , $H-19$ H=0.21, $Ha-22$ , $Ha-30$ H=0.21, $Ha-22$ , $Ha-21$ , $Ha-22$ H=0.21, $Ha-22$ , $Ha-30$ H=0.21, $Ha-22$ , $Ha-21$ , $Ha-22$ H=0.21, $Ha-22$ , $Ha-21$ , $Ha-22$ H=0.21, $Ha-22$ , $Ha-21$ , $Ha-22$ H=0.21, $Ha-20$ H=0.21,	15	00.72	Ū	H <b>β</b> -12 1.36 m		$H_2 = 11, H_{\alpha} = 12$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	13	39.25	S		H-8, H <sub>2</sub> -11, H <b>a</b> -12, H-18, H <sub>3</sub> -26, H <sub>3</sub> -27	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	14	39.62	s		H\$-7, H-8, H-18, H3-26, H3-27	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	15	29.38	t	H <sub>2</sub> -15 1.25 m	H-8, H2-16, H3-26	$H_2 - 16$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	16	32.65	t	H <sub>2</sub> -16 1.49 m	H <b>β-22, H3-28</b>	H2-15
18 54.46 d H-18 1.48 d (2.0) Ha-12, Hb-21, Ha-22, H-19 (2.0) H <sub>3</sub> -27, H <sub>3</sub> -28 H-18, H-20, Ha-21 H <sub>3</sub> -29, H <sub>3</sub> -30 H <sub>3</sub> -29, H <sub>3</sub> -30 20 35.96 d H-20 1.49 m H-18, H <sub>3</sub> -29, H <sub>3</sub> -30 H <sub>3</sub> -29, H <sub>3</sub> -30 21 27.85 t Ha-21 1.44 m H-18, H <sub>3</sub> -29, H <sub>3</sub> -30 H <sub>3</sub> -29, H <sub>3</sub> -30 22 42.44 t Ha-22 1.25 m H-18, H <sub>3</sub> -28 Ha-21, Hβ-22 Hb-21 1.67 m Ha-21, Hβ-22 H-19, Hb-21, Ha-22 Hb-21 1.67 m Ha-21, Hβ-22 H-22 Ha-21, Hβ-22 Ha-21, Hβ-22 Ha-21, Hβ-22 Ha-21, Hβ-22 Ha-21, Hβ-22 Ha-21, Hβ-22 Ha-21, Hβ-22 Ha-22 Ha-21, Hβ-22 Ha-21, Hβ-22 Ha-22 Ha-21, Hβ-22 Ha-22 Ha-21, Hβ-22 Ha-21, Hβ-22 Ha-22 Ha-21, Hβ-22 Ha-22 Ha-21, Hβ-22 Ha-21, Hβ-22 Ha-22 Ha-21, Hβ-22 Ha-21, Hβ-22 Ha-22 Ha-21, Hβ-22 Ha-22 Ha-21, Hβ-22 Ha-22 Ha-22 Ha-21, Hβ-22 Ha-22 Ha-22 Ha-22 Ha-22 Ha-22 Ha-21, Hβ-22 Ha-22	17	39.92	S		H <sub>2</sub> -15, H <sub>2</sub> -16, Hb-21 Hβ-22, H <sub>3</sub> -28	
19 48. 24 d H-19 1. 57 m Hb-21, H $\alpha$ -22, H-18, H-20, Ha-21 13 25. 96 d H-20 1. 49 m H-18, H_3-29, H_3-30 H_3-29, H_3-30 21 27. 85 t Ha-21 1. 44 m H-18, H_3-29, H_3-30 H_3-29, H_3-30 Hb-21 1. 67 m H-18, H-20, H $\beta$ -22 H-19, Hb-21, H $\alpha$ -22 22 42. 44 t H $\alpha$ -22 1. 25 m H-18, H_3-28 Ha-21, H $\beta$ -22 H $\beta$ -22 1. 79 dd (11. 5, 9. 0) 23 27. 26 q H_3-23 1. 04 s H_3-24 Ha-21, H $\alpha$ -22 Hb-21, H $\alpha$ -22 24 25. 39 q H_3-24 1. 13 s H_3-23 25 28. 77 q H_3-25 0. 90 s H $\beta$ -1, H-8, H-10, H $2$ -11, H $\alpha$ , $\beta$ -12 26 15. 39 q H_3-26 0. 80 s H $\beta$ -1, H-8, H-10, H $2$ -11, H $\alpha$ , $\beta$ -12 26 15. 39 q H_3-26 0. 80 s H $\beta$ -1, H-8, H $\beta$ -12, H-18 28 33. 35 q H_3-28 0.93 s H $2$ -16, H-18, H $\alpha$ , $\beta$ -22 29 21. 32 q H_3-29 0. 87 d H_3-30 H-20 (6. 8) 30 2. 3. 44 q H_3-30 0. 90 d H_3-29 H-20	18	54.46	đ	H-18 1.48 d (2.0)	Hα-12, Hb-21, Hα-22, H <sub>3</sub> -27, H <sub>3</sub> -28	H-19
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	19	48.24	d	H-19 1.57 m	Hb-21, H $\alpha$ -22, H <sub>3</sub> -29, H <sub>3</sub> -30	H-18, H-20, Ha-21
21 27.85 t $Ha-21$ 1.44 m $H-18$ , $H-20$ , $H\beta-22$ $H-19$ , $Hb-21$ , $H\alpha-22$ $Hb-21$ 1.67 m $Ha-21$ , $H\beta-22$ 22 42.44 t $H\alpha-22$ 1.25 m $H-18$ , $H_3-28$ $Ha-21$ , $H\beta-22$ $H\beta-22$ 1.79 dd $H\beta-22$ 1.79 dd $Hb-21$ , $H\alpha-22$ $H\beta-22$ 1.79 dd $Hb-21$ , $H\alpha-22$ $H\beta-22$ 1.79 dd $Hb-21$ , $H\alpha-22$ $H\beta-22$ 1.79 dd $Hb-21$ , $H\alpha-22$ $Hb-21$ , $H\alpha-22$ Ha-20 (6.8) Ha-20 (6.8) Ha-20 (6.0)	20	35.96	d	H-20 1.49 m	H-18, H <sub>3</sub> -29, H <sub>3</sub> -30	H <sub>3</sub> -29, H <sub>3</sub> -30
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	21	27.85	t	Ha-21 1.44 m	H-18, H-20, H <b>β-22</b>	H-19, Hb-21, H <b>a</b> -22
22 42. 44 t $H\alpha - 22$ 1. 25 m $H^{-18}$ , $H_3 - 28$ $Ha - 21$ , $H\beta - 22$ $H\beta - 22$ 1. 79 dd $Hb - 21$ , $H\alpha - 22$ (11. 5, 9. 0) 23 27. 26 q $H_3 - 23$ 1. 04 s $H_3 - 24$ 24 25. 39 q $H_3 - 24$ 1. 13 s $H_3 - 23$ 25 28. 77 q $H_3 - 25$ 0. 90 s $H\beta - 1$ , $H-8$ , $H^{-10}$ , $H_2 - 11$ , $H\alpha, \beta - 12$ 26 15. 39 q $H_3 - 26$ 0. 80 s $H^{-8}$ , $H_2 - 15$ $H^{-8}$ 27 16. 78 q $H_3 - 27$ 0. 88 s $H_2 - 11$ , $H\beta - 12$ , $H^{-18}$ 28 33. 35 q $H_3 - 28$ 0. 93 s $H_2 - 16$ , $H^{-18}$ , $H\alpha, \beta - 22$ 29 <sup>e</sup> 21. 32 q $H_3 - 29$ 0. 87 d $H_3 - 30$ $H^{-20}$ 30 <sup>e</sup> 23. 44 q $H_3 - 30$ 0. 90 d $H_3 - 29$ $H^{-20}$				Hb-21 1.67 m		Ha-21, H <b>β</b> -22
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	22	42.44	t	Har-22 1.25 m	H-18, H <sub>3</sub> -28	Ha-21, H <b>β</b> -22
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				H <b>g</b> -22 1.79 dd		Hb-21, H <b>a</b> -22
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		07 00		(11.5, 9.0)	11 D.4	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	23	27.26	q	$H_3 = 23$ 1.04 S	$H_3 - 24$	
25 28.77 q $H_3 - 25 0.90$ s $H_{\beta} - 1, H - 3, H - 10, H_{2} - 11, H\alpha, \beta - 12$ 26 15.39 q $H_3 - 26 0.80$ s $H - 8, H_{2} - 15$ $H - 8$ 27 16.78 q $H_{3} - 27 0.88$ s $H_{2} - 11, H\beta - 12, H - 18$ 28 33.35 q $H_{3} - 28 0.93$ s $H_{2} - 16, H - 18, H\alpha, \beta - 22$ 29 21.32 q $H_{3} - 29 0.87$ d $H_{3} - 30$ $H - 20$ (6.8) 30 e 23.44 q $H_{3} - 30 0.90$ d $H_{3} - 29$ $H - 20$ (6.0)	24	25.39	q	H3-24 1.13 S	$H_3 - 23$	
26 15.39 q H <sub>3</sub> -26 0.80 s H-8, H <sub>2</sub> -15 H-8 27 16.78 q H <sub>3</sub> -27 0.88 s H <sub>2</sub> -11, H $\beta$ -12, H-18 28 33.35 q H <sub>3</sub> -28 0.93 s H <sub>2</sub> -16, H-18, H $\alpha,\beta$ -22 29 <sup>e</sup> 21.32 q H <sub>3</sub> -29 0.87 d H <sub>3</sub> -30 H-20 (6.8) 30 <sup>e</sup> 23.44 q H <sub>3</sub> -30 0.90 d H <sub>3</sub> -29 H-20 (6.0)	25	28.77	đ	пз-25 0.90 S	пр-1, н-8, н-10, H <sub>2</sub> -11. Н <b>а</b> .8-12	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	26	15.39	a	H1-26 0.80 s	$H-8, H_2-15$	H-8
28 33.35 $q$ H <sub>3</sub> -28 0.93 s H <sub>2</sub> -16, H-18, H $\alpha, \beta$ -22 29 <sup>e</sup> 21.32 $q$ H <sub>3</sub> -29 0.87 d H <sub>3</sub> -30 H-20 (6.8) 30 <sup>e</sup> 23.44 $q$ H <sub>3</sub> -30 0.90 d H <sub>3</sub> -29 H-20 (6.0)	$\bar{27}$	16.78	ā	H <sub>3</sub> -27 0.88 s	$H_2 - 11$ , $H_{\beta} - 12$ , $H - 18$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	28	33.35	a	H <sub>3</sub> -28 0.93 s	$H_2 = 16$ , $H = 18$ , $H\alpha$ . $\beta = 22$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	29 <b>e</b>	21.32	ą	H <sub>3</sub> -29 0.87 d	H <sub>3</sub> -30	H-20
$30^{\circ}$ 23.44 q H <sub>3</sub> -30 U.90 a H <sub>3</sub> -29 H-20 (6.0)		00.44		(6.8)		11.00
	306	23.44	đ	H <sub>3</sub> -30 U.90 d (6.0)	H3-29	H-20

Table 1. NMR Data for 1<sup>a</sup>

a) Spectra were taken on a Varian XL-400 ( $^{1}$ H, 400 MHz;  $^{13}$ C, 100.6 MHz) in CDCl<sub>3</sub>. b)  $^{1}$ H- $^{13}$ C (one-bond) COSY. Figures in parentheses are coupling constants. c)  $^{1}$ H- $^{13}$ C (long-range) COSY. d)  $^{1}$ H- $^{1}$ H COSY. e) These are exchangeable.

and 1.59, 1.42 (H<sub>2</sub>-1) were respectively observed in the  $^1\mathrm{H-}^1\mathrm{H}$  COSY spectrum.

The EIHRMS displayed characteristic fragments at m/z 152.1205 (152.1201 for C<sub>10</sub> H<sub>16</sub> O) (a) and 274.2648 (274.2660 for C<sub>20</sub> H<sub>34</sub>) (b) arising from a retro-Diels-Alder fission<sup>4</sup> (Scheme 1). Thus, these findings and the NMR data pointed out a 25,26-dinor-9,13-dimethyllup-5-en-3-ol for 1.

Assuming that rings A, C and D respectively adopt a chair form and ring B a half-chair form, the differences in NOE experiments assigned B/C cis, C/D trans and D/E cis to the ring fusions in 1 (Scheme 1). The orientation of  $Pr^{i}$ -19 could not be decided by NOE experiments.

An X-ray analysis of 1 completely proved the above-deduced stereochemistry to be correct (Figure 1).<sup>5</sup> The orientation of  $Pr^{i}$ -19 was



Figure 1. ORTEP-view of X-ray structure of 1

determined to be  $\alpha$ .

It is known that 3-dehydrodesoxogratiogenin (2)<sup>6</sup> and alnusenone (3)<sup>7</sup> show a negative Cotton effect at 295 nm ( $n \rightarrow \pi^{*}$ ) in the CD spectra. 3-Dehydrohancokinol (4),<sup>8</sup> derived from 1, exhibited a negative Cotton effect at 295 nm and the same curve at 325-249 nm as those of 2 and 3. Thus, the absolute stereochemistry of 1 can be determined to be the 3*S*, 8*R*, 9*S*, 10*S*, 13*R*, 14*S*, 17*S*, 18*S*, 19*S*-configuration.

## References and Notes

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- EIHRMS m/z: M<sup>+</sup>, 426.3862 (426.3862 for C<sub>30</sub>H<sub>50</sub>O). Anal. Calcd for C<sub>30</sub>H<sub>50</sub>O: C, 84.40; H, 11.81. Found: C, 84.17; H, 11.71.
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- The crystal data were: 1, C<sub>30</sub>H<sub>50</sub>O, Mol. Wt. =426.68, Tetragonal, space 5. group I4. Z=8. Lattice constants, a=b=26.272 (4), c=7.4892 (8)Å, V=5169.2Å<sup>3</sup>, Dcalc=1.091 g/cm<sup>-3</sup>,  $\mu$  for CuK $\alpha$ =0.589 cm<sup>-1</sup>. A total of 1285 reflections were messured as being above the  $3\sigma$  (I) level in the  $2\theta$  range of  $0-150^{\circ}$ . The crystal structure was elucidated by the direct method and atomic parameters were refined by block-diagonal least squares procedure. The final R value was 0.074 for 1142 reflections including 41 hydrogen atoms for which isotropic thermal The final atomic parameters have been parameters were applied. deposited with Cambridge Crystallographic Data Center. The details will be presented elsewhere.
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- 8. This compound was obtained by oxidation of 1 with PDC. Colorless needles, mp 115-117° (MeOH),  $[\alpha]_{D}^{20}$  +17.2° (c=0.50, CHCl<sub>3</sub>), +17.6° (c=0.50, dioxane). IR (CHCl<sub>3</sub>): 1702 cm<sup>-1</sup> (CO). CD  $[\theta]^{20}$  (nm): 0 (325), -2120 (314) (sh), -3990 (303) (negative maximum), -3940 (300) (positive maximum), -4100 (295) (negative maximum), -2120 (275) (sh), 0 (249), +24200 (212) (positive maximum) (c=0.84×10<sup>-3</sup>, dioxane). EIHRMS  $m \times z$ : M<sup>+</sup>, 424.3704 (424.3704 for C<sub>30</sub>H<sub>48</sub>O).

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