

SCHISANLACTONE B, A NEW TRITERPENOID FROM A SCHISANDRA SP.

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Abstract: Schisanlactone B, a triterpenoid isolated from a Schisandra sp., is shown to have structure 2.

In the preceding paper,¹ we reported the structure of schisanlactone A (1), a triterpenoid isolated from an unidentified Schisandra sp. indigenous to the Hubei province of China. We report herein the structure of schisanlactone B, obtained from the same source.¹

Schisanlactone B (2), C₃₀H₄₂O₄ (M⁺ 466.3074), mp 205—207°, [α]_D²⁰ +80.2° (c 0.94, CHCl₃), like schisanlactone A,¹ possesses two unsaturated lactone rings as indicated by IR (1715 cm⁻¹ for six membered and 1675 cm⁻¹ for seven-membered α,β -unsaturated lactones), ¹H NMR (see Table 1) and ¹³C NMR (see Table 2). However, schisanlactone B has only four olefinic carbons and thus must have one ring more than schisanlactone A. The UV spectrum ($\lambda_{\text{max}}^{\text{MeOH}}$ 251 nm (log ϵ 4.15)) indicates that one of the unsaturated lactones is further conjugated. The appearance of only six methyl groups (¹H NMR), along with the presence of a pair of one-proton doublets at δ 1.05 and δ 1.24, suggests the presence of a cyclopropane ring. Conjugation of the cyclopropane ring with the A-ring lactone accounts for the UV peak at 251 nm^{2,3} and leads to structure 2, which is consistent with the NMR spectrum. The high field position (δ 0.81) of H-6_{ax} and the low field position (δ 1.87) of H-6_{eq} are accounted for by the shielding and deshielding effects, respectively, of the cyclopropane ring.⁴ The low field position (δ 2.07) of H-11_{ax} and the cyclopropane hydrogens are due to deshielding by the ring A double bond.

The stereochemistry shown in 2 was further confirmed by measurement of nuclear Overhauser effects (shown in Table 3), by selective ¹H-¹H decoupling experiments (which confirm the coupling assignments in Table 1), and the ¹³C NMR data shown in Table 2. Schisanlactone B shows a negative Cotton effect at 240 nm (Δ_{ϵ} -7.07) in its CD spectrum, opposite to that of schisanlactone A¹, and thus is tentatively assigned the (S)-configuration at C-22.⁶

TABLE 1. ^1H NMR parameters of schisanlactone B^a

Proton ^b	Chemical Shift	^1H - ^1H coupling constants
H-1	6.14	$J_{1,2} = 12.65$
H-2	5.95	$J_{1,2} = 12.65$
H-5 _{ax}	2.42	$J_{5ax,6ax} = 13.11$; $J_{5ax,6eq} = 4.57$
H-6 _{ax}	0.81	$J_{5ax,6ax} = 13.11$; $J_{6ax,6eq} = 12.91$; $J_{6ax,7ax} = 11.16$; $J_{6ax,7eq} = 3.64$
H-6 _{eq}	1.87	$J_{6ax,6eq} = 12.91$; $J_{6eq,7ax} = 4.59$; $J_{6eq,5ax} = 4.57$; $J_{6eq,7eq} = 4.41$
H-7 _{ax}	1.23	$J_{6ax,7ax} = 11.16$; $J_{6eq,7ax} = 4.59$; $J_{7ax,7eq} = 13.24$; $J_{7ax,8ax} = 10.89$
H-7 _{eq}	1.49	$J_{6eq,7eq} = 4.41$; $J_{6ax,7eq} = 3.64$; $J_{7eq,8ax} = 5.99$; $J_{7eq,7ax} = 13.24$
H-8 _{ax}	1.80	$J_{7ax,8ax} = 10.89$; $J_{7eq,8ax} = 5.99$
H-11 _{ax} [*]	2.07	$J_{11ax,12ax} = 13.64$; $J_{11ax,12eq} = 6.84$
H-11 _{eq} [*]	1.57~1.64	$J_{11eq,12ax} = 6.62$, $J_{11eq,12eq} = 6.84$
H-12 _{ax}	1.69	$J_{11ax,12ax} = 13.64$; $J_{11eq,12ax} = 6.62$
H-12 _{eq}	1.70	$J_{11eq,12eq} = 6.84$; $J_{11ax,12eq} = 6.84$
H-15 _α [*]	1.57~1.64	
H-15 _β [*]	1.78	
H-16 _α , 16 _β [*]	1.34~1.40	
H-17 _α [*]	1.57~1.64	
H-18	0.97	
H-19A	1.24	$J_{19A,19B} = 5.05$
H-19B	1.05	$J_{19A,19B} = 5.05$
H-20 [*]	2.04	$J_{20,21} = 6.08$; $J_{20,22} = 3.50$
H-21	0.98	$J_{20,21} = 6.08$
H-22	4.47	$J_{20,22} = 3.50$; $J_{22,23A} = 13.14$; $J_{22,23B} = 3.45$
H-23A [*]	2.38	$J_{22,23A} = 13.14$; $J_{23A,23B} = 14.0$; $J_{23A,24} = 1.54$; $J_{23A,27} = 2.0$
H-23B [*]	2.10	$J_{22,23B} = 3.45$; $J_{23A,23B} = 14.0$; $J_{23B,24} = 6.48$; $J_{23B,27} < 0.5$
H-24	6.62	$J_{23A,24} = 1.54$; $J_{23B,24} = 6.48$; $J_{24,27} < 0.5$
H-27	1.92	$J_{23A,27} = 2.0$; $J_{23B,27} < 0.5$; $J_{24,27} < 0.5$
H-28, H-29	0.90, 1.38	
H-30	1.36	

^aChemical shift (CDCl_3) in ppm, relative to internal TMS, coupling constants in Hz. All parameter values were attained by first-order approximation at 400 MHz (Bruker WH-400). ^bThe assignments are on the basis of ^1H - ^1H selective decoupling experiments. *Overlapping signals. Some coupling constants are assigned directly from the coupling partners and some are obtained by ^1H - ^1H selective decoupling.

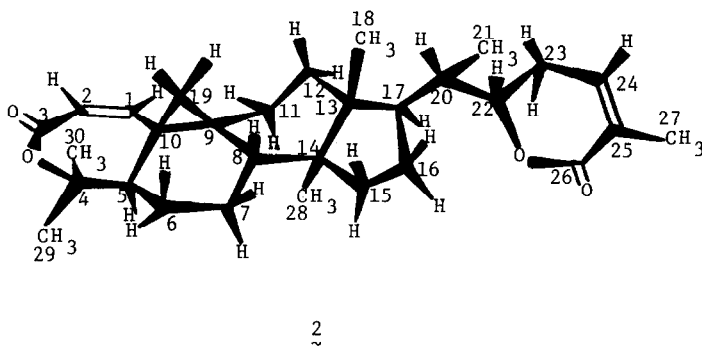
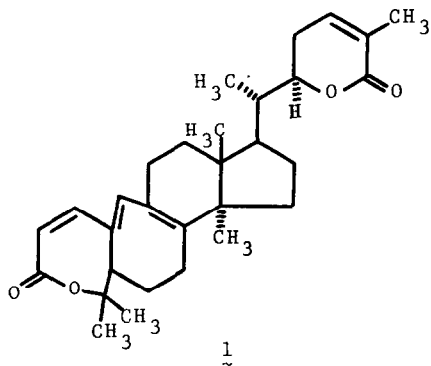


TABLE 3. Results of NOE enhancement studies on schisanlactone B*

Irrid.	Obser.	NOE(%)	Conclusions	Irrid.	Obser.	NOE(%)	Conclusions	
H-29	H-5 _{ax}	6.2	H-5 _{ax} , H-6 _{eq} , H-7 _{ax} , H-28, H-15 _α , H-11 _{ax} , H-29 are <u>syn</u> and <u>α</u> . C-30 is close to O, C-4, C-5 plane.	H-6 _{ax}	H-19A	2.7	H-18A is <u>endo</u> .	
	H-6 _{eq}	5.9			H-6 _{eq}	8.7		
H-30	H-5 _{ax}	7.4			H-8 _{ax}	2.5	H-18, H-19A, H-18B, H-8 _{ax} , H-6 _{ax} , H-12 _{ax} , H-15 _β , H-16 _β , H-22, H-20, H-23B are <u>syn</u> and β.	
H-6 _{eq}	H-6 _{ax}	11.1			H-18	H-8 _{ax}		12.2
	H-5 _{ax}	4.1			H-12 _{ax}	10.9		
H-28	H-5 _{ax}	4.2			H-16 _β	H-15 _β	16.0	
	H-11 _{ax}	5.0			H-22	H-22	6.2	
	H-15 _α	8.0		H-22	H-16 _β	5.9		
	H-7 _{ax}	4.2			H-23B	4.0		
H-1	H-2	13.8			H-20	4.0		
	H-11 _{ax}	4.3		H-21	H-23A	6.5	H-21, H-23A are <u>syn</u> in preferred conformation	
	H-11 _{eq}	6.6						
	H-19B	4.1	H-19B is <u>exo</u> .	H-18	H-20	20.0	H-18, H-20 are <u>syn</u> in preferred conformation	
H-19B	H-1	2.5						
	H-19A	7.2		H-28	H-24	9.0		

*Measured in CDCl₃ on a Bruker WH-400 spectrometer.

TABLE 2. ^{13}C NMR chemical shifts of schisanlactone B^a

Carbon	Chemical Shift	Carbon	Chemical Shift	Carbon	Chemical Shift	Carbon	Chemical Shift
C-1	150.44	C-9	33.47	C-17	48.11	C-24	139.24
C-2	120.49	C-10	28.68	C-18	16.96	C-25	128.49
C-3	167.33	C-11*	32.14	C-19	24.05	C-26	166.43
C-4	84.52	C-12	32.55	C-20	39.23	C-27	17.18
C-5	46.38	C-13**	48.71	C-21	13.18	C-28	18.99
C-6	24.45	C-14**	45.57	C-22	80.48	C-29	29.24
C-7*	28.98	C-15*	26.92	C-23	23.60	C-30	22.08
C-8	45.07	C-16	35.02				

^aIn CDCl_3 , chemical shifts in ppm relative to internal TMS, determined at 100 MHz on a WH-400 spectrometer. The assignments are based on $\{^1\text{H}\}\text{-}^{13}\text{C}$ single frequency selective decoupling with multiplicity determined by ^{13}C spin-echo with gated ^1H decoupling.⁵ *,**May be interchanged.

References

1. J.-S. Liu, M.-F. Huang, G.F. Arnold, E. Arnold, J. Clardy, and W.A. Ayer, Tetrahedron Letters, preceding paper.
2. J.P. Phillips, Spectra-Structure Correlation, Academic Press, New York, London, 1964, p. 34.
3. D.S. Irvine, J.A. Henry, and F.S. Spring, J. Chem. Soc., 1316 (1955).
4. L.M. Jackman and S. Sternhell, Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd ed. Pergamon Press, Toronto, 1969, p. 98.
5. D.W. Brown, T.T. Nakashima, and D.L. Rabenstein. J. Magn. Reson. **45**, 302 (1981).
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