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Studies on Constituents of Medicinal Plants. XVII.[1] Constituents of *Schizandra nigra* Max. and Their Carbon-13 Nuclear Magnetic Resonance Spectra. (2)

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A new sesquiterpene keto alcohol named schizandronol has been isolated from the wooden part of *Schizandra nigra* Max. and structure I has been proposed on the basis of chemical and spectral evidences. The carbon-13 nuclear magnetic resonance spectra of schizandronol and oplodiol were studied. β-Sitosterol, schizandrolic acid and oplodiol have also been isolated.

Previously, the authors have isolated schizandronic acid from the methanol-soluble fraction of the wooden part of *Schizandra nigra* Max. and elucidated its structure.[3] Further investigation on the constituents of this plant has led to the isolation of a new sesquiterpene keto alcohol. This paper concerns the structural elucidation of the sesquiterpene to be named schizandronol hereafter and the analyses of carbon-13 nuclear magnetic resonance (NMR) spectra of schizandronol and oplodiol.[4] The methanolic extract, after separation of schizandronic acid,[3] afforded β-sitosterol, schizandrolic acid,[3] oplodiol[4] and schizandronol (I), $C_{15}H_{22}O_2$, colorless needles of mp 110°, $[\alpha]_D^{19}$ =−105° ($CHCl_3$, c=1.00). The ultraviolet (UV) spectrum of I exhibits the UV maximum at 237 nm (log ε 3.97), assignable to an α,β-unsaturated carbonyl group with two alkyl substituents, and the infrared (IR) spectrum of I exhibits IR bands at 3300 (OH), at 1670 (α,β-unsaturated C=O) and at 895 cm^{-1} (exocyclic methylene). The NMR spectrum (Table I) indicates that I has an isopropyl group, a primary alcohol group, an exocyclic methylene group, and an olefinic proton which resonates at rather low magnetic field (7.05) and appears as a singlet. Schizandronol (I) yielded monoacetate (II) $C_{17}H_{24}O_3$ of mp 77—78° on treatment with acetic anhydride and pyridine, but efforts to prepare tosylate of I failed and the starting material (I) was lost almost completely, suggesting that I has a primary allylic alcohol group[5] in the molecule. Schizandronol (I), on reduction in the presence of palladium-charcoal in ethanol, afforded a liquid (III) (M^+=222). The IR spectrum of III does not exhibit bands due to hydroxyl, exocyclic methylene, and α,β-unsaturated C=O groups, but exhibits a band at 1710 cm^{-1}, assignable to a six-membered ring C=O group. The NMR spectrum of III exhibits signals due to an isopropyl group and two $-\overset{|}{C}H-CH_3$ groups. The liquid (III) yielded crystalline oxime (IV) $C_{15}H_{27}ON$ of mp 110° and yielded, on reduction with $LiAlH_4$, colorless needles, $C_{15}H_{28}O$ (V) of mp 107—108°, which shows IR band due to a hydroxyl group and NMR signals due to an isopropyl group, a hydroxyl group, and two $-\overset{|}{C}H-CH_3$ groups. The NMR signal of the methine proton of a newly formed HC–OH group of V at 3.10 (m, $W_h/_2$=22 Hz) indicates that the hydroxyl group is equatorial. The selenium dehydrogenation of V afforded a liquid(VI), the UV spectrum of which was similar to that of cadalene.[6] The IR spectra of VI and cadalene[6,7] were almost superimposable.

1) Part XVI: Y. Tanabe, R. Shinoda, Y. Horikoshi, and K. Takahashi, *Yakugaku Zasshi*, **96**, 248 (1976).
2) Location: *13-1 Takaramachi, Kanazawa, 920, Japan.*
3) K. Takahashi and M. Takani, *Chem. Pharm. Bull.* (Tokyo), **23**, 538 (1975).
4) H. Minato and M. Ishikawa, *J. Chem. Soc.*, **1967**, 423.
5) P.S. Kalsi and I.S. Bhata, *Perfumery Ess. Oil Record*, **1967**, 84, 295.
6) B.A. Nagasampagi, S. Dev, C. Rai, and K.L. Murthy, *Tetrahedron*, **22**, 1949 (1966).
7) K. Adachi, *Yuki Gosei Kagaku Kyokaishi*, **27**, 875 (1969).

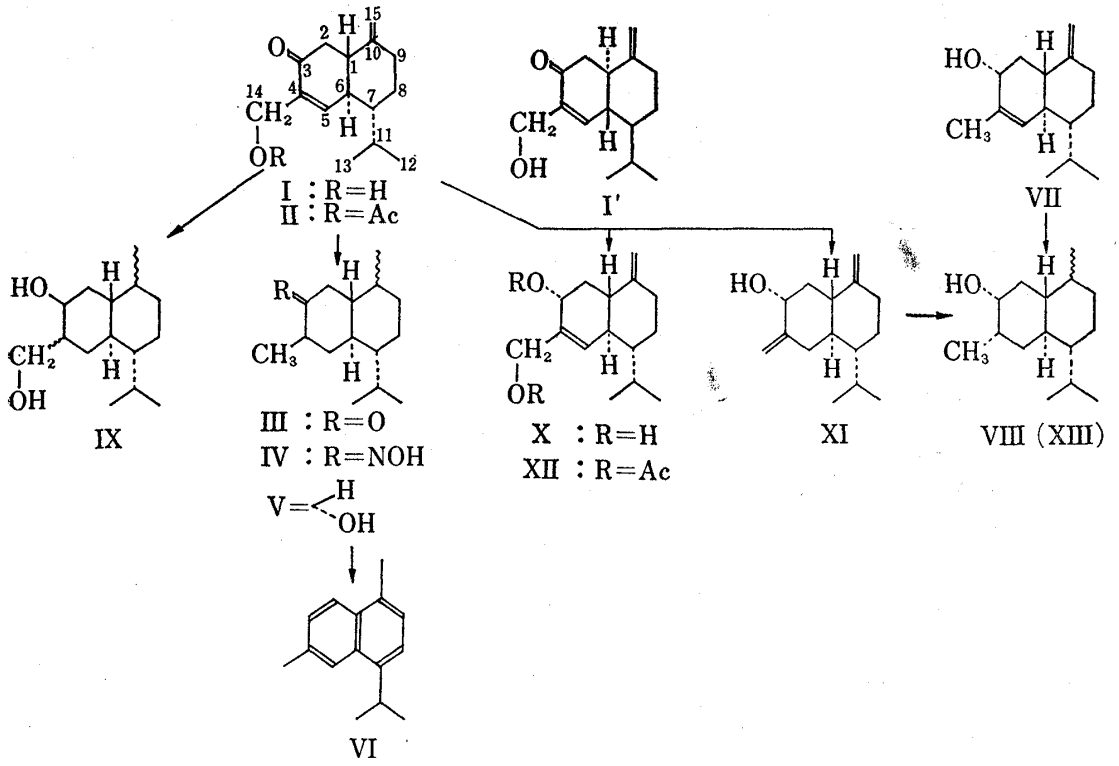

Chart 1

The picrate of VI, $C_{21}H_{21}O_7N_2$, yellow needles of mp 110—112°, was proved to be identical with an authentic sample of cadalene picrate[7] by the mixed fusion and IR comparison. These chemical and spectral evidences suggest that schizandronol (I) is cadinane type of sesquiterpene keto alcohol which has an exocyclic methylene group and a trisubstituted double bond carrying $-CH_2OH$ group. The NMR signals of I at 4.53 (s, 1H) and 4.76 (s, 1H) suggest that the exocyclic methylene group does not exist in conjugation with a carbonyl group, because an exocyclic methylene group in conjugation with a carbonyl group usually resonates at lower magnetic field (5.96, 5.75).[8] The NMR signal of the olefinic proton of I at rather low magnetic field (7.05, s) indicates that the olefinic proton exists at β-position of the α,β-unsaturated carbonyl group and that dihedral angle between the proton and the proton at an adjacent carbon is approximately 90°, a requirement satisfied by the *trans*-fused structure.[9] The isopropyl group of I might be of equatorial rather than of axial which is less stable, as in the case of khusinol.[10] These evidences indicate that schizandronol (I) could be formulated as I or I', as shown in Chart 1. With regard to cyclohexenone with planar chromophore, when the C-atom that sticks out of the plane of the ring is in the negative Octant, the sign of the circular dichroism is positive and *vice versa*.[11] The C_1- atom of I which sticks out of the plane of the ring is in the positive Octant and the C_1- atom of I' in the negative Octant. Schizandronol shows the negative Cotton effect on the optical rotatory dispersion (ORD) curve,[12] indicating that schizandronol could be formulated as I. The compound III shows the positive Cotton effect on the ORD,[13] also suggesting that schizandronol is I-type of compound. In confirmation of this conclusion, the NMR spectra of V and tetrahydro-derivative $C_{15}H_{28}O$ (VIII) of synthetically established cadin-4,10(15)-diene-3α-ol[9] (VII) were studied. (Table I).

8) S. Hayashi, A. Matsuo, and T. Matsuura, *Tetrahedron Letters*, **1969**, 1599.
9) R.B. Kelly and J. Eber, *Can. J. Chem.*, **50**, 3272 (1972).
10) S.V. Tirodkar, S.K. Paknikar, and K.K. Chakravarti, *Sci. Cul.*, **35**, 27 (1969).
11) G. Snatzke, *Tetrahedron*, **21**, 413, 421 (1965).
12) C. Djerassi and J.E. Gurst, *J. Am. Chem. Soc.*, **86**, 1755 (1964).
13) W. Moffitt, R.B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Am. Chem., Soc.*, **83**, 4013 (1961).

Recently it has become possible to calculate the chemical shift of the carbinol protons of substituted cyclohexanols of known conformation by using basic shift values for the equatorial and axial protons and additive parameters for various alkyl substituents on the ring.[14] The axial carbinol protons (equatorial alcohol) at C_3 of V and VIII resonate at 3.10 and 3.76, respectively. The difference (0.66 ppm) between the chemical shift values is equal to the difference (0.66 ppm) between the chemical shift value of the axial carbinol hydrogen of 2(equ)-methylhexanol (parameter for equatorial methyl group is −28 Hz at 60 MHz) and that of 2(ax)-methylhexanol (parameter for axial methyl group is +11.5 Hz at 60 MHz).[14] These spectral evidences indicate that the conformation of the methyl group at C_4 of V is equatorial (β) and that of the methyl group at C_4 of VIII is axial (α).

Table I. The ^{1}H-NMR Data (δ-value, ppm in $CDCl_3$, J in Hz, 100 MHz)

	Me\CH- and Me-CH-, Me/(=C-CH$_3$)	CH_2OR	CH_2=	CHOR	-CH=	OH(OAc)
I	0.81, d, 3H (J=7) 1.01, d, 3H (J=7)	4.29, s, a) 2H	4.53, s, a) 4.76, s, a) each signal: 1H		7.05, s, a) 1H	2.54, s, 1H
II	0.83, d, 3H (J=7) 1.02, d, 3H (J=7)	4.75, s, a) 3H	4.55, s, a) 1H		7.10, s, a) 1H	(2.09, s, 3H)
III	0.74, 0.81:3H 0.87, 0.94:6H 0.98, 1.04:3H					
IV	0.71, 0.78:3H 0.86, 0.93, 0.98:6H 1.09, 1.15:3H					8.10, br, 1H
V	0.67, 0.74:3H 0.84, 0.91:6H 0.98, 1.04:3H			3.10, m, 1H $W_{h/2}$=22		1.50, s, 1H
IX	0.71, 0.78:3H 0.80, 0.87, 0.93:6H	3.74, m, 2H		4.22, m, 1H $W_{h/2}$=7		2.28, s, 2H
X	0.77, d, 3H (J=7) 0.95, d, 3H (J=7)	4.28, br, 2H	4.60, m, 2H 4.72, s, a) 1H		5.92, s, a) 1H	2.60, br
XII	0.77, d, 3H (J=7) 0.92, d, 3H (J=7)	4.30, 4.42, 4.72, 4.84, q, 2H	4.52, s, a) 4.70, s, a) each signal: 1H	5.58, 1H $W_{h/2}$=16, t-like	6.08, s, a) 1H	(2.03, s, 3H), (2.05, s, 3H)
XI	0.71, d, 3H (J=7) 0.92, d, 3H (J=7)		4.51, s, a) 4.63, s, a) 4.77, s, a) 4.90, s, a) each signal: 1H	4.11, q, 1H (J=5 and 11)		1.72, s, 1H
XIII	0.68, 0.75:3H 0.83, 0.88, 0.90, 0.95:9H			3.76, 1H $W_{h/2}$=20		1.50, s, 1H
VII	0.74, d, 3H (J=7) 0.93, d, 3H (J=7) (1.79, s, a) 3H)		4.58, s, a) 4.69, s, a) each signal: 1H	4.23, 1H $W_{h/2}$=18, t-like	5.65, s, a) 1H	1.64, s, 1H
VIII	0.68, 0.75:3H 0.83, 0.88, 0.90, 0.95:9H			3.76, m, 1H $W_{h/2}$=20		1.50, s, 1H

a) s: slightly dull
abbreviation: br=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet

Schizandronol (I), on reduction in the presence of Adams catalyst in acetic acid, afforded $C_{15}H_{28}O_2$ (IX) of mp 140—141°, which exhibits NMR signals due to the C_3- proton at 4.22 (m, 1H, $W_{h/2}$=7 Hz), indicating that the OH group at C_3 of IX is axial (β). Schizandronol (I) gave, by reduction with $LiAlH_4$, colorless plate $C_{15}H_{24}O_2$ (X) of mp 165—166° and colorless needles $C_{15}H_{24}O$ (XI) of mp 95—96°. The IR and NMR spectra of X indicate that the reduc-

14) E.L. Eliel, M.H. Gianni, Th H. Williams, and J.B. Stothers, *Tetrahedron Letters*, **1962**, 741; S.H. Schroeter and E.L. Eliel, *J. Org. Chem.*, **30**, 1 (1965).

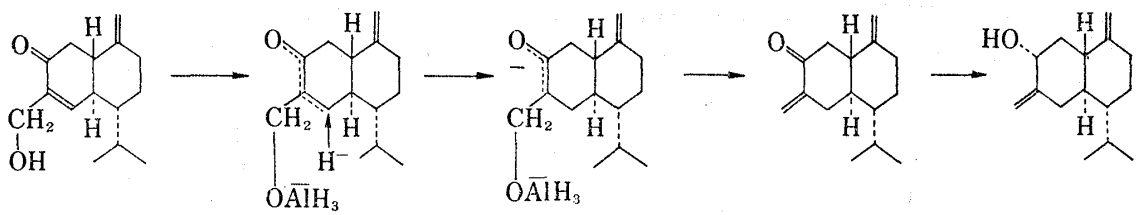

Chart 2

tion converted the C=O group of I to –CHOH group, which could be assumed to have an equatorial OH group (α), because the acetate (XII) of X shows the NMR signals due to the methine proton of the –CHOAc group at 5.58 (t-like, 1H, $W_h/_2$=16 Hz). The compound (XI) shows the IR band at 3400 cm^{-1} (OH) and the NMR signals due to an isopropyl group, two exocyclic methylene group, and a –CHOH group whose methine proton at 4.11 (q, 1H, J=5 and 11 Hz) could be assumed to be axial (β), but XI does not exhibit NMR signal due to $-CH_2OH$ and –CH= groups, indicating that the allylic alcohol group of I might be converted into an exocyclic methylene group through the mechanism[15] as shown in Chart 2. The compound (XI), on reduction in the presence of Adams catalyst in acetic acid, afforded $C_{15}H_{28}O$ (XIII) of mp 107°. The NMR spectrum of XIII in $CDCl_3$ was identical with that of a racemic sample of VIII, mp 92.5—93°, prepared from a totally synthetic VII[9] by hydrogenation. Identity of the relative stereochemistry of both samples was also supported by their identical TLC behavior. In the solid state both samples showed IR absorption bands at identical positions within the spectral range under experimental observation, but with slightly different relative absorbances in the region of 1320—1290 and 970—980 cm^{-1}. However, because of the extremely small quantity of material VIII isolated the techniques available for identification were limited to those discussed above. These spectral and chemical evidences indicate that I, II, III, IV, V, VI, VIII, IX, X, XI, XII and XIII could be formulated as shown in Chart 1.

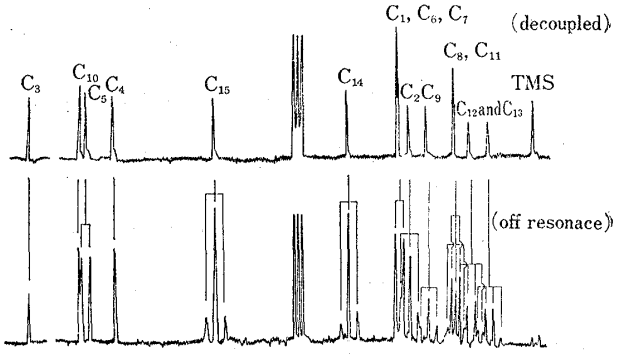

Fig. 1. The ^{13}C-NMR Spectra of Schizandronol (I). (in $CDCl_3$, 25.15 MHz)

Table II. Carbon-13 Shieldings in Schizandronol (I). (in $CDCl_3$, ppm from TMS, 25.15 MHz)

	C_{13} and C_{12}		C_8, C_{11}		C_9	C_2	C_1, C_6, C_7	C_{14}	C_{15}	C_4[a]	C_5	C_{10}[a]	C_3
Decoupled	15.2,	21.4	26.4		35.4	41.5	44.8, 45.1	61.8	105.5	137.9	147.4	149.4	200.5
	q	q	t	d	t	t	d	t	t	s	d	s	s
Off resonance	10.9	17.4	23.5,	25.2	32.7	38.8	43.7	59.0	105.5	137.9	146.2	149.4	200.5
	13.8	20.1	26.4	27.7	35.5	41.6	46.4	61.8			149.0		
	16.6	22.8	29.3		38.0	44.2		64.6					
	19.5	25.2											

a) The assignments of the signals might have to be reversed.

15) A.S. Dreiding and J.A. Hartman, *J. Am. Chem. Soc.*, **75**, 939 (1953).
16) L.P. Lindeman and J.Q. Adams, *Anal. Chem.*, **43**, 1245 (1971); D.E. Dorman, M. Jautelat, and J.D. Roberts, *J. Org. Chem.*, **36**, 2757 (1971).

The carbon-13 NMR spectrum of I could be interpreted[16] as shown in Fig. 1 and Table II. The carbon-13 NMR spectrum of oplodiol[4] could be interpreted[16,17] as shown in Fig. 2 and Table III.

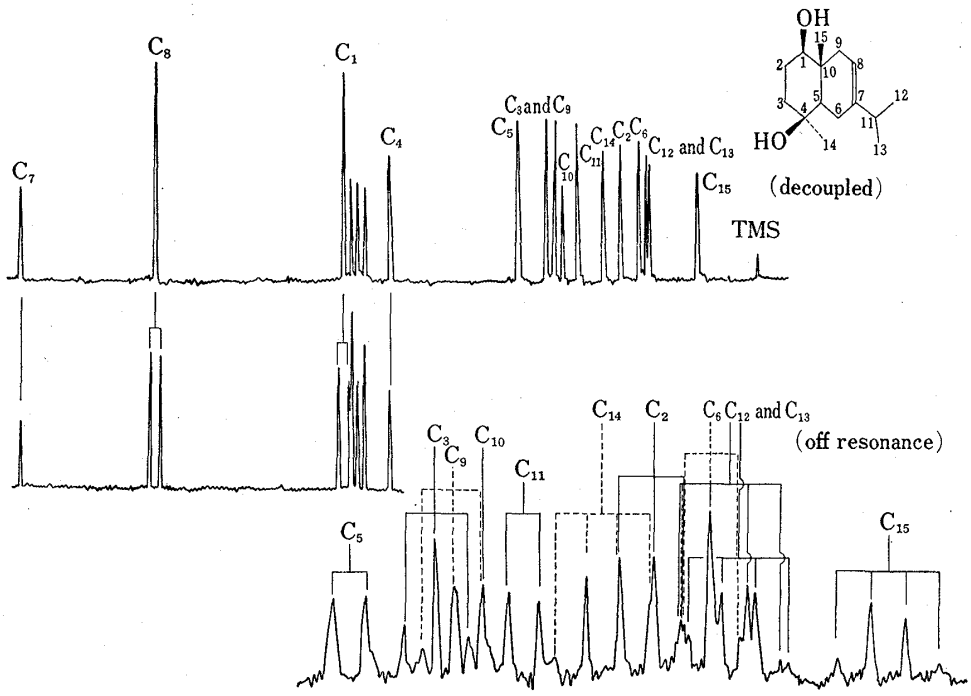

Fig. 2. The ^{13}C-NMR Spectra of Oplodiol (in $CDCl_3$, 25.15 MHz)

TABLE III. Carbon-13 Shieldings in Oplodiol (in $CDCl_3$, ppm from TMS, 25.15 MHz)

	C_{15}	C_{12} and C_{13}	C_6	C_2	C_{14}	C_{11}	C_{10}	C_9[a]	C_3[a]	C_5	C_4	C_1	C_8	C_7
Decoupled	11.8	21.3, 21.8	23.1	26.7	29.7	35.0	37.6	39.5	40.7	46.3	70.9	79.8	116.1	141.8
	q	q q	t	t	q	d	s	t	t	d	s	d	d	s
Off resonance	8.5	18.1, 18.6,	21.2	24.5	26.8	34.0	37.6	37.6	38.6	45.2	70.9	78.7	114.9	141.8
	10.6	20.2, 20.7,	22.9	26.7	28.8	35.9		39.5	40.7	47.2		80.7	117.1	
	12.8	22.3, 22.9,	24.5	28.8	30.9			41.5	42.7					
	14.9	24.3, 24.9,			33.0									

a) The assignments of the signals are ambiguous and might have to be reversed.

Experimental

The following instruments were used for obtaining physical data. Melting points: Yanagimoto Micro-melting Apparatus (a hot-stage type), and recorded uncorrected: UV spectra: Hitachi 323 recording spectro meter in ethanol; IR spectra: Nippon Bunko IR-G spectrometer in KBr; ^1H and ^{13}C NMR spectra (tetramethylsilane as internal standard, δ-value): JNM-PS-100 high resolution instrument in $CDCl_3$ at 100 MHz and 25.15 MHz, respectively, mass(MS) spectra: JMS-OISG mass spectrometer (direct inlet, 75 eV); ORD spectra: Nippon Bunko Optical Dispersion Curve Recorder ORD/UV-5; Optical rotation: Nippon Bunko polarimeter DIP-SL. Thin-layer chromatography (TLC) was performed on glass-plates coated with silica gel and following solvent systems were used: solvent A ($CHCl_3$–MeOH=100: 1), solvent B (benzene–AcOEt=5: 1), solvent C (benzene–AcOEt=50: 1), solvent D ($CHCl_3$–MeOH=50: 1) and solvent E (benzene–AcOEt=20: 1). Spots were visualized by spraying conc.H_2SO_4, followed by heating.

Schizandronol (I)——Dried cut wooden part (15 kg) of *Schizandra nigra* was extracted with methanol and the extract was chromatographed on a column of silica gel (2.5 kg) with *n*-hexane and benzene, successively. The *n*-hexane- and benzene-soluble fractions were chromatographed over silica gel with solvent A. The fraction (*Rf* 0.32, TLC, solvent A) afforded schizandronic acid[3] of mp 167—168° (mixed fusion and

17) S.H. Grover and J.B. Stothers, *Can. J. Chem.*, **52**, 870 (1974).

IR comparison) and the fraction (*Rf* 0.51, TLC, solvent A) afforded β-sitosterol of mp 140° (mixed fusion and IR). The fraction (*Rf* 0.42, TLC, solvent A) afforded schizandronol, colorless needles (I) of mp 110° on recrystallization from ether–petr. ether. Yield. 2.2 g. *Anal.* Calcd. for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found. C, 76.60; H, 9.26. IR ν_{max} cm^{-1}: 3300 (OH), 1670 (α,β-unsatd. C=O), 1640 (C=C), 1385, 1370 (isopropyl), 3070, 895 (exocyclic methylene). ORD (c=0.17, dioxane, 17°): $[\phi]_{500}=-468$, $[\phi]_{400}=-1216$, $[\phi]_{375}=-2714$, $[\phi]_{365}=-2246$, $[\phi]_{360}=-2433$, $[\phi]_{338}=0$, $[\phi]_{320}=+1170$, $[\phi]_{285}=0$, $[\phi]_{250}=-2808$.

Schizandrolic Acid——The fraction (*Rf* 0.16, TLC, solvent A) (0.5 g) afforded schizandrolic acid[3] of mp 165° (mixed fusion and IR). *Anal.* Calcd. for $C_{30}H_{48}O_3$: C, 78.89; H, 10.50. Found. C, 78.37; H, 10.24.

Oplodiol——The column eluted with solvent A mentioned above was then eluted with acetone and the acetone-soluble fraction was chromatographed over silica gel with solvent B. The fraction (*Rf* 0.18, TLC, solvent B) afforded oplodiol,[4] colorless needles of mp 107—108° from pet-ether. (mixed fusion and IR). Yield: 350 mg. *Anal.* Calcd. for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. Found. C, 75.69; H, 10.92. $[\alpha]_D^{27°}=-58.0$ (c=1.00, $CHCl_3$). NMR (δ-value): 0.98 (s, 3H, C_{15}-CH_3), 1.04 (d, 6H, J=7 Hz, isopropyl), 1.19 (s, 3H, C_{14}-CH_3), 1.41 (s, 2H, OH), 3.33 (q, 1H, J=4 and 11 Hz, C_1-H), 5.34 (m, 1H, C_8-H). Oplodiol was acetylated with pyridine and acetic anhydride to give acetate of mp 70—71°. *Anal.* Calcd. for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06. Found. C, 72.77; H, 9.83. $[\alpha]_D^{24}=-30.0°$ (c=1.05, $CHCl_3$). NMR (δ-value): 1.03 (d, 6H, J=6 Hz, isopropyl), 1.06 (s, 3H, C_{15}-CH_3), 1.20 (s, 3H, C_{14}-CH_3), 1.25 (s, 1H, OH), 2.07 (s, 3H, OAc), 4.55 (q, 1H, J=4 and 11 Hz, C_1-H), 5.27 (m, 1H, C_8-H).

Acetylation of I——A solution of I (150 mg) in pyridine (1 ml) and acetic anhydride (1.5 ml) was allowed to stand for 18 hr at room temperature and treated as usual to give colorless triangular crystals (II) of mp 77—78° from MeOH–H_2O. Yield: 110 mg. *Anal.* Calcd. for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.42; H, 8.66. IR ν_{max} cm^{-1}: 1735 (OAc), 1675 (α,β-unsatd. C=O), 1640 (C=C), 1230, 1025 (–C–O–C–), 3070, 895 (exocyclic methylene).

Catalytic Hydrogenation of I with Pd-C——Schizandronol (I) (500 mg) in ethanol (10 ml) was hydrogenated over 10% Pd-C (250 mg). When 188 ml of H_2 was absorbed, the mixture was filtered. The filtrate was chromatographed over silica gel with benzene. The fraction (*Rf* 0.53, TLC, benzene) afforded a liquid (III). ORD (c=0.13, MeOH): $[\phi]_{500}=153.1$, $[\phi]_{350}=768.1$, $[\phi]_{310}=1946.9$ (peak), $[\phi]_{288}=0$, $[\phi]_{274}=-512.8$ (through) $[\phi]_{250}=0$, $[A]=+24.60$. IR ν_{max} cm^{-1}: 1710 (ring C=O), 1380, 1370 (isopropyl).

Oxime of III——The compound III (20 mg) was added to a solution of NH_2OH. HCl (10 mg), AcONa (10 mg) in EtOH (10 ml) and the mixture was warmed on a steam-bath for 3 hr. After evaporation of ethanol, the residue was chromatographed over silica gel with solvent C. The fraction (*Rf* 0.28, TLC, solvent C) afforded colorless needles (IV) of mp 110° on recrystallization from ethanol. Yield: 7 mg. IR ν_{max} cm^{-1}: 3250 (OH), 1660 (C=N), 1380, 1370 (isopropyl), 945 (N-O). *Anal.* Calcd. for $C_{15}H_{27}ON$: C, 75.89; H, 11.47; N, 5.90. Found: C, 75.86; H, 11.26; N, 5.78.

$LiAlH_4$ Reduction of III——A solution of III (30 mg) in dry ether (5 ml) was added dropwise to a solution of $LiAlH_4$ (60 mg) in dry ether (5 ml) and the mixture was heated for 4 hr. Under ice cooling, water and dil. H_2SO_4 were added to it and the mixture was extracted with ether. The ether-soluble fraction was chromatographed over silica gel with solvent C. The fraction (*Rf* 0.23, TLC, solvent C) was sublimated at 60° under 1 mmHg pressure to afford colorless needles (V) of mp 107—108°. Yield: 15 mg. *Anal.* Calcd. for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found. C, 79.99; H, 13.04. IR ν_{max} cm^{-1}: 3350 (OH), 1380, 1370 (isopropyl), 1040 (C-O).

Selenium-Dehydrogenation of V——A mixture of V (250 mg), Se (500 mg) and linoleic acid (4 drops) was heated at 280—285° for 13 hr in the stream of N_2 gas. After filtration of Se, the reaction mixture was chromatographed over silica gel with *n*-hexane. The fraction (*Rf* 0.64, TLC, *n*-hexane) afforded cadalene (VI). $M^+=198$. UV λ_{max} (nm, log ε): 228.5 (4.64), 280.5 (3.69, sh), 284.0 (3.71), 291 (3.72), 323 (2.74, sh), 326 (2.84). IR ν_{max} cm^{-1}: 1625, 1600 (benzene ring), 1380, 1360 (isopropyl), 825, 805, 780 (benzene protons). The compound VI afforded yellow needles of picrate of mp 110—112°, which was proved to be identical with an authentic sample[7] of cadalene picrate. *Anal.* Calcd. for $C_{21}H_{21}O_7N_3$: C, 59.01; H, 4.95; N, 9.83. Found: C, 59.50; H, 4.93; N, 9.92.

Catalytic Hydrogenation of I with PtO_2——Schizandronol (I) (300 mg) in acetic acid (5 ml) was hydrogenated over PtO_2 (100 mg). When 127 ml of H_2 was absorbed, the mixture was filtered. The filtrate was chromatographed over silica gel with solvent D. The fraction (*Rf* 0.41, TLC, solvent D) afforded colorless needles (140 mg) (IX) of mp 140—141° from pet-ether. *Anal.* Calcd. for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 75.00; H, 11.94. IR ν_{max} cm^{-1}: 3300 (OH), 1375, 1365 (isopropyl), 1040, 1020 (C-O).

$LiAlH_4$-Reduction of I——Schizandronol (I) (500 mg) in dry ether (30 ml) was added dropwise to a suspension of $LiAlH_4$ (850 mg) in dry ether (50 ml) and the mixture was refluxed for 11 hr and then the mixture was poured into ice-cold dil. H_2SO_4 and then extracted with ether. The ether-soluble fraction was chromatographed over silica gel with solvent D. The fraction (*Rf* 0.83, TLC, solvent D) afforded colorless needles (XI) of mp 95—96° from pet-ether. Yield: 120 mg. IR ν_{max} cm^{-1}: 3400 (OH), 1655, 1640 (C=C), 1385, 1370 (isopropyl), 1020 (C-O), 3080, 895, 890 (exocyclic methylene). *Anal.* Calcd. for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.63; H, 10.70. The fraction (*Rf* 0.29, TLC, solvent D) afforded colorless plates (X) of mp 165—166° from acetone. Yield: 260 mg. IR ν_{max} cm^{-1}: 3350, 3300 (OH), 1640, 840 (trisubstituted double bond), 3070, 890 (exocyclic methylene), 1040 (C-O), 1005 (C-O). *Anal.* Calcd. for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24. Found: C, 76.23; H, 10.07.

Acetylation of X——A mixture of X (65 mg), pyridine (1 ml) and acetic anhydride (1 ml) allowed to stand overnight and then poured into water and extracted with $CHCl_3$. The $CHCl_3$-soluble fraction was chromatographed over silica gel with benzene. The fraction (*Rf* 0.16, TLC, benzene) afforded a liquid (XII). Yield: 48 mg. IR ν_{max} cm^{-1}: 1740, 1235, 1025 (OAc), 1645, 845 (trisubstituted double bond), 1370 (isopyl), 3080, 890 (exocyclic methylene). Mass Spectrum *m/e* (relative intensity): 320 (12) (M^+), 278 (27) (M^+-$COCH_2$), 270 (10), 260 (72) (M^+-AcOH), 223 (39), 218 (100) (260-$COCH_2$), 205 (25), 200 (59) (260-AcOH), 185 (9), 175 (47), 157 (99) (200-isopropyl), 131 (26), 130 (12), 129 (17), 118 (12), 117 (13), 105 (17), 104 (16), 91 (20), 79 (11), 69 (11).

Catalytic Hydrogenation of Cadin-4,10 (15)-diene-3α-ol (VII)——The compound VII (15 mg) in acetic acid was hydrogenated over Adams catalyst (5 mg). When 13 ml of H_2 gas was absorbed, the mixture was filtered. The filtrate was chromatographed over silica gel with solvent E. The fraction (*Rf* 0.27, TLC, solvent E) (V shows a spot at *Rf* 0.31 under the same condition) was sublimated at 60° under 1 mmHg pressure to give colorless needles (VIII) of mp 92.5—93°. Yield: 5 mg. It shows a spot at *Rf* 0.19 (TLC, solvent C) and at *Rf* 0.68 (TLC, solvent D). IR ν_{max} cm^{-1}: 3300 (OH), 1380, 1360 (isopropyl), 1040 (C–O). Mass Spectrum *m/e* (relative intensity): 224 (8) (M^+), 206 (50) (M^+-H_2O), 191 (5) (206-CH_3), 163 (100) (206-isopropyl), 150 (30), 137 (10), 135 (7), 121 (17), 107 (38), 92 (28), 69 (15), 67 (12).

Attempted Tosylation of I——A mixture of I (100 mg) in dry pyridine (0.5 ml) and tosyl chloride (120 mg) in pyridine (1.5 ml) was allowed to stand for 90 hr at room temperature. Then the mixture was poured into ice water and extracted with ether and $CHCl_3$, successively. Neither I nor its tosylate was isolated from both ether and $CHCl_3$ layers.

Catalytic Hydrogenation of XI——The compound XI (25 mg) in acetic acid (3 ml) was hydrogenated over Adams catalyst (8 mg). When 14 ml of H_2 gas was absorbed, the mixture was filtered and the filtrate was chromatographed over silica gel with solvent C. The fraction (*Rf* 0.19, TLC, solvent C) was sublimated at 70° under 1 mmHg pressure to give colorless needles (XIII) of mp 107°. Yield: 10 mg. It shows a spot at *Rf* 0.27 (TLC, solvent E) and at *Rf* 0.68 (TLC, solvent D). IR ν_{max} cm^{-1}: 3300 (OH), 1380, 1360 (isopropyl), 1040 (C-O). *Anal.* Calcd. for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.01; H, 13.00.

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