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Studies on Constituents of Medicinal Plants. X.[1] The Nuclear Magnetic Resonance (NMR) Spectra of Dihydropaulownin and Dihydrosesamin and a Revised Structure for Isopaulownin

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1) Dihydropaulownin (VI) $C_{20}H_{20}O_7$, mp 125°, dihydropaulownin acetate (VII) $C_{22}H_{22}O_8$, mp 105—106°, dihydrosesamin (II) $C_{20}H_{20}O_6$, mp 98—99° and dihydrosesamin acetate (III) $C_{22}H_{22}O_7$, mp 91—93° were prepared.
2) The NMR spectra of II, III, VI and VII were studied.
3) The Mass spectra of VIII and XI were studied.
4) The structure of isopaulownin was revised as X.

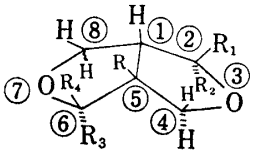
The lignan paulownin $C_{20}H_{18}O_7$[3] mp 105—106° has been shown to have structure (I) by the analysis of the NMR spectrum.

This paper will deal with the NMR spectra of dihydrosesamin (II) and dihydropaulownin (VI) and a revised structure (X) for isopaulownin. Dihydrosesamin $C_{20}H_{20}O_6$ (II) mp 98—99° was newly obtained from *d*-sesamin by partial hydrogenolysis with palladium-charcoal. It gave acetate $C_{22}H_{22}O_7$ (III) mp 91—93° by acetylation with pyridine and acetic anhydride. By thorough hydrogenolysis with sodium in liquid ammonia or by catalytic hydrogenolysis with palladium-charcoal, paulownin (I) gave tetrahydropaulownin $C_{20}H_{22}O_7$ (V), mp 166—167°. By partial hydrogenolysis with sodium in liquid ammonia or palladium-charcoal, it gave dihydropaulownin $C_{20}H_{20}O_7$ (VI) mp 125°, $[\alpha]_D = -9.2°$ ($c=0.974$, $CHCl_3$), which gave monoacetate $C_{22}H_{22}O_8$ (VII), mp 105—106° by acetylation with pyridine and acetic anhydride.

The NMR Spectra of Dihydrosesamin (II) and Its Acetate (III)

The NMR spectra could be interpreted to accord with structures (II) and (III) for them respectively, as shown in Table I. The absence of a signal due to a methyl group rejects the structure (IV) for dihydrosesamin. The methylene protons of CH_2OH at C_5 of II and of CH_2-OAc at C_5 of III are assumed to be magnetically non-equivalent by the restricted rotation between the CH_2OH or CH_2OAc groups at C_5 and the CH_2-aryl group at C_1 and exhibit signals

1) Part IX: K. Takahashi, M. Ogura and Y. Tanabe, *Chem. Pharm. Bull.* (Tokyo), 17, 2223 (1969).
2) Location: *Takaramachi, Kanazawa.*
3) K. Takahashi and T. Nakagawa, *Chem. Pharm. Bull.* (Tokyo), 14, 641 (1966).



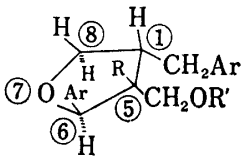
I : R = OH, R_1 = R_4 = Ar, R_2 = R_3 = H

VIII : R = OAc, R_1 = R_4 = Ar, R_2 = R_3 = H

IX : R = OH, R_1 = R_3 = Ar, R_2 = R_4 = H

X : R = OH, R_2 = R_4 = Ar, R_1 = R_3 = H

XI : R = OAc, R_2 = R_4 = Ar, R_1 = R_3 = H

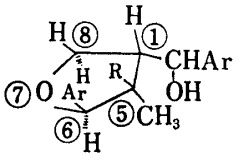


II : R = H, R' = H

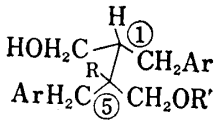
III : R = H, R' = Ac

VI : R = OH, R' = H

VII : R = OH, R' = Ac



IV : R = H



V : R = OH, R' = H

Ar : 3,4-methylenedioxyphenyl

Chart 1

TABLE I. NMR Signals of Dihydrosesamin (II) and Its Acetate (III) (J in cps, in $CDCl_3$ and D_2O, 100 Mc)

Assignment	II τ values	Multiplicity	No. of protons	δ_A	δ_B	J_{AB}	J_{AX}	J_{BX}
C_6–H	5.24, 5.29	d	1				5	
C_8–H	5.95, 6.01, 6.03, 6.09	q	1	6.03			6	
	6.27, 6.32, 6.35, 6.40	q	1		6.33	8		5
C_5–CH_2	6.13, 6.19, 6.23, 6.29	q	1	6.23			6	
	6.29, 6.35, 6.39, 6.45	q	1		6.35	10		6
OH	8.08	s	1					
C_1–H, C_5–H, C_1–CH_2	7.09—7.78	m	4					
CH_2(O–, O–)	4.12	s	4					
Aromatic–H	3.22—3.47	m	6					

Assignment	III τ values	Multiplicity	No. of protons	δ_A	δ_B	J_{AB}	J_{AX}	J_{BX}
C_6–H	5.24, 5.30	d	1				6	
C_8–H	5.89, 5.95, 5.97, 6.03	q	1	5.97			6	
	6.25, 6.31, 6.33, 6.39	q	1		6.32	8		6
C_5–CH_2	5.60, 5.67, 5.71, 5.78	q	1	5.71			7	
	5.78, 5.86, 5.89, 5.97	q	1		5.85	11		8
$OCOCH_3$	7.99	s	3					
C_1–H, C_5–H, C_1–CH_2	7.11—7.66	m	4					
CH_2(O–, O–)	4.09	s	4					
Aromatic–H	3.20—3.45	m	6					

abbriviation: s, singlet, d, doublet, t, triplet, q, quartet, m, multiplet

of ABX type by coupling with the methine proton at C_5. The difference (0.51 ppm) between the chemical shift (6.29 τ) of the methylene protons of CH_2OH group at C_5 of II and that (5.78 τ) of the methylene protons of CH_2OAc at C_5 of III might be due to the magnetic effect of acetyl group on III.

The NMR Spectra of Dihydropaulownin (VI) and Its Acetate (VII)

Four structures for dihydro-compounds of I could be considered. The absence of a signal of a methyl group rejects two structures with a methyl group in the molecule for dihydropaulownin. The fact that the same dihydro-compound is obtained from I and isopaulownin (X) indicates that dihydropaulownin should be formulated as VI. Dihydropaulownin acetate could be considered to have structure (VII), because it was obtained from VI by acetylation with pyridine and acetic anhydride and the chemical shift (7.98 τ) of the acetyl group of CH_2OAc at C_5 of VII is nearly equal to that (7.99 τ) of the acetyl group of CH_2OAc at C_5 of III and, as compared with the chemical shift (6.325 τ) of the methylene protons of CH_2OH group at C_5 of VI, the chemical shift (5.83 τ) of the methylene protons of CH_2OAc at C_5 of VII is shifted diamagnetically by 0.495 ppm which is almost equal to the value 0.51 ppm, observed in the case of II and III. The methylene protons of the CH_2OH group at C_5 of VI exhibit a quartet of

Table II. NMR Signals of Dihydropaulownin (VI) and Its Acetate (VII) (in $CDCl_3$, 100 Mc)

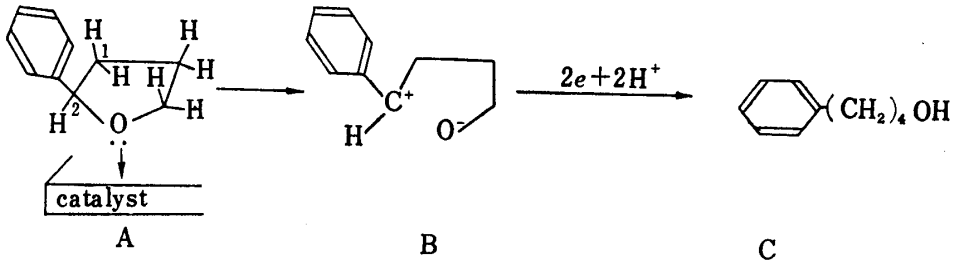
Assignment	VI							
	τ values	Multiplicity	No. of protons	δ_A	δ_B	J_{AB}	J_{AX}	J_{BX}
C_6–H	5.21	s	1					
C_8–H	5.81, 5.87, 5.89, 5.95	q	1	5.88		8	6	
	6.29, 6.34, 6.37, 6.42	q	1		6.35			5
C_5–CH_2	6.14, 6.24	d	1	6.20		10		
	6.41, 6.51	d	1		6.45			
C_1–CH_2	6.93, 6.95, 7.05, 7.07	q	1	7.01		12	2	
	7.53, 7.65	d[b]	1		7.59			b)
C_5–CH_2OH	7.80	s	1					
C_5–OH	8.25	s	1					
C_1–H	7.33—7.65	m	1					
$CH_2<^{O-}_{O-}$	4.07	s	2					
	4.09	s	2					
Aromatic-H	3.19—3.44	m	6					

Assignment	VII							
	τ values	Multiplicity	No. of protons	δ_A	δ_B	J_{AB}	J_{AX}	J_{BX}
C_6–H	5.25	s	1					
C_8–H	5.84,[a] 5.90, 5.93, 5.99	q[a]	1	5.92		9	6	
	6.34, 6.39, 6.43, 6.48	q	1		6.41			5
C_5–CH_2	5.83	s	2					
C_1–CH_2	7.05, 7.07, 7.16, 7.18	q	1	7.12		11	2	
	7.53, 7.64	d[b]	1		7.58			b)
C_5–OH	8.28	s	1					
$OCOCH_3$	7.98	s	3					
C_1–H	7.30—7.64	m	1					
$CH_2<^{O-}_{O-}$	4.14	s	2					
	4.16	s	2					
Aromatic-H	3.22—3.50	m	6					

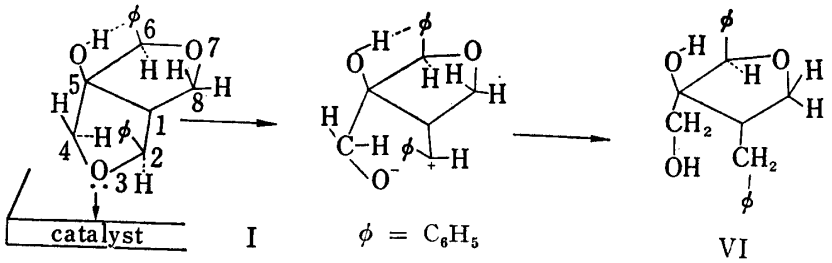
a) The signal was overapped with the signals of the methylene protons of CH_2OH at C_5.
b) The proton appeared in a doublet, probably because J_{BX} is small.

AB type by the restricted rotation mentioned above, but the methylene protons of the CH_2OAc group at C_5 of VII exhibit a singlet, probably because the different anisotropic effects of the OH group at C_5 on each of the non-equivalent methylene protons might make the methylene protons magnetically equivalent. The NMR spectra of dihydropaulownin and its acetate could be interpreted to accord with the structures VI and VII for them respectively, as shown in Table II.

The mechanism for catalytic hydrogenolysis of 2-aryltetrahydrofuran derivatives, postulated by Mitsui and Saito,[4] involves an intermediate (A) where the oxygen atom of the furan ring is bonded to the catalyst surface. The electron-releasing aryl group of the intermediate (A), far from the catalyst surface, serves to cleave the C_2–O bond in a manner similar to S_N1 reaction, and the resulting intermediate (B) is reduced to the hydrogenolised product (C).



In the hydrogenolysis of paulownin, the C_5–OH group seems to render the hydrogenolytic cleavage of the C_6–O_7 bond less favorable than that of the C_2–O_3 bond by an electronic interaction with π-electrons of the aryl group at the 6-position which decreases the electron-releasing effect of the aryl group.



Even if the hydrogenolysis of paulownin would have involved an intermediate where both aryl group and oxygen atom are bonded to the catalyst surface, a steric interaction between C_5–OH group and C_6-aryl group would also be less favorable for the formation of such an intermediate leading to cleavage at C_6–O_7.

The NMR Spectra of Paulownin Acetate (VIII), Isopaulownin (X) and Its Acetate (XI)

The analyses of the NMR spectra of II, III, VI and VII, mentioned above, indicate that tetrahydrofuran derivatives such as II and VI do not always obey the Karplus law. Recently Birch, *et al.*[5] have reported that the coupling constant between C_1–H and C_2–H of gmelinol is not indicative of the stereochemistry, the Karplus law not being obeyed.[6] So it seems to be necessary to reinvestigate the stereochemistry of isopaulownin. Isopaulownin was previously[3] assumed to be formulated as IX due to the fact that the doublet at 4.87 τ (1H, J=5 cps) in the NMR spectrum indicates the presence of the proton at C_2 in axial and of the methine proton at C_1 in equatorial comformations, the coupling constant J=5 cps being almost equal to that of asarinin J=4.8 cps ($J_{equ.C_1\text{-}H\text{-}ax.C_2\text{-}H}$, *trans*). It was also assumed that the conversion took place at C_6, providing that the spin–spin coupling obeys the Karplus law.

4) K. Mitsui and H. Saito, *Nippon Kagaku Zasshi*, **81**, 289 (1960).
5) A.J. Birch, P.L. Macdonald and A. Pelter, *J. Chem. Soc.* (*C*), **1967**, 1968.
6) L.H. Zalkow and M. Ghosal, *Chem. Commun.*, **18**, 922 (1967).

The methylene protons at C_4 and C_8 of VIII, X and XI could now be interpreted as shown in Table III and IV. The NMR analyses of I and X indicate that the axial proton of the methylene protons at C_8 of X exhibits the signals at a higher magnetic field (6.72 τ) than that (6.21 τ) of the axial proton at C_8 of I, suggesting that the axial proton of the methylene protons at C_8 and the aryl group at C_2 of X are both in axial comformation and the axial proton is within the shielding cone of the aromatic ring of aryl group at C_2. The shielding (6.16 τ—6.39 τ to 6.50 τ—6.82 τ) was observed in the case of VIII and XI. These NMR analyses and the chemical evidence that I and X gave VI mentioned above, indicate that isopaulownin should be formulated as X.

In the previous paper,[3] the multiplet (7.00 τ, center, 2H) in the NMR spectrum of *d*-sesamin was assigned to the methine protons at C_1 and C_5. The unusual chemical shift of the methine proton was comfirmed by the spin–spin decoupling experiment as shown in Table V, proving that the proton on the carbon β to the oxygen in the fused tetrahydrofurofuran ring has an unusual chemical shift.

The Mass Spectra of VIII and XI

Whilst intensity difference are found between the spectra, the overall patterns are so similar that no stereochemical assignments could be made with safety.[7] Some of the fragmentations could be analysed as shown in Chart 2 and Table VI.

Table III. NMR Signals of Paulownin (I) and Isopaulownin (X) (in $CDCl_3$ and D_2O, 60 Mc)

Assignment	I: τ values	Multiplicity	No. of protons	δ_A	δ_B	J_{AB}	J_{AX}	J_{BX}
C_2–H	5.15, 5.23	d	1				4.8	
C_6–H	5.23	s	1					
C_4–H	5.89, 6.05	d	1	6.01				
	6.09, 6.24	d	1		6.13	9.3		
C_8–H (eq.)	5.39, 5.53, 5.67	t	1	5.53			8.0	
C_8–H (ax.)	6.09, 6.18, 6.24, 6.34	q	1		6.21	9.0		5.5
C_1–H	6.87—7.18	m	1					
C_5–OH	8.12	s	1					
$CH_2\langle^{O-}_{O-}$	4.05	s	4					
Aromatic-H	3.07—3.20	m	6					

Assignment	X: τ values	Multiplicity	No. of protons	δ_A	δ_B	J_{AB}	J_{AX}	J_{BX}
C_2–H	4.83, 4.91	d	1				5.0	
C_6–H	5.51	s	1					
C_4–H	5.78, 5.93	d	1	5.87				
	6.29, 6.44	d	1		6.35	9.0		
C_8–H (eq.)	5.94, 6.07, 6.08, 6.21	q	1	6.08			7.8	
C_8–H (ax.)	6.59, 6.72, 6.73, 6.86	q	1		6.72	8.4		7.8
C_1–H	6.86—7.08	m	1					
C_5–OH	8.25	s	1					
$CH_2\langle^{O-}_{O-}$	4.03	s	4					
Aromatic-H	3.10—3.22	m	6					

7) A. Pelter, *J. Chem. Soc.* (*C*), **1967**, 1376.

Table IV. NMR Signals of Paulownin Acetate (VIII) and Isopaulownin Acetate (XI) (in $CDCl_3$)

Assignment	VIII (60 Mc) τ values	Multiplicity	No. of protons	δ_A	δ_B	J_{AB}	J_{AX}	J_{BX}
C_2–H	5.27, 5.35	d	1				4.8	
C_6–H	5.00	s	1					
C_4–H	5.48, 5.67	d	1	5.62				
	5.74, 5.93	d	1		5.79	11.4		
C_8–H	5.48, 5.59, 5.63, 5.74	q	1	5.62			6.6	
	6.16, 6.24, 6.31, 6.39	q	1		6.27	9.0		4.8
C_1–H	6.61—6.89	m	1					
$OCOCH_3$	8.27	s	3					
CH_2<O– O–	4.07	s	2					
	4.10	s	2					
Aroamtic-H	3.08—3.24	m	6					

Assignment	XI[a] (100 Mc) τ values	Multiplicity	No. of protons	δ_A	δ_B	J_{AB}	J_{AX}	J_{BX}
C_2–H	4.90, 4.95	d	1				5.0	
C_6–H	5.36	s	1					
C_4–H	5.39, 5.50	d	1	5.45				
	5.98, 6.09	d	1		6.03	11.0		
C_8–H	5.98—6.26	m	1					
C_1–H	6.50—6.82	m	2					
$OCOCH_3$	8.25	s	3					
CH_2<O– O–	4.07	s	2					
	4.09	s	2					
Aromatic-H	3.17—3.33	m	6					

a) The mp 142—143° was erroneously reported as 105° in the previous paper.[3]

Table V. NMR Signals of *d*-Sesamin (in $CDCl_3$, 60 Mc)

Assignment	*d*-Sesamin τ-values	Multiplicity	No. of protons	*d*-Sesamin, irradiated at 7.00 τ τ-values	Multiplicity	No. of protons
C_2,C_6–H	5.32, 5.39	d	2	5.29	s	2
C_4,C_8–H	5.68, 5.80, 5.83, 5.95	q	2	5.67, 5.82	d	2
	6.10, 6.16, 6.25, 6.31	q	2	6.05, 6.19	d	2

Experimental

The NMR spectra were measured by a Varian A-100 or A-60 spectrometer in $CDCl_3$ or $CDCl_3$ and D_2O solutions, with tetramethylsilane as an internal standard. The mass spectra were measured by JMS-01SG mass spectrometer, the ionizing current kept at 200 μA, while the ionizing energy being maintained at 75 eV and the source temperature at 110°.

Hydrogenolysis of *d*-Sesamin with Palladium-Charcoal——A solution of 0.5 g of *d*-sesamin and Pd-C (prepared from 5 ml of 1% palladium chloride and 0.1 g of carbon) in 20 ml of tetrahydrofuran was shaken in H_2 stream for 15 min. After absorption of 39 ml of H_2, the catalyst was removed off and the solvent was distilled off to give crystalline substance, which was purified by the thin-layer chromatography (TLC) (dry method) as follows: The substance, after drying completely, dissolved in a minimum volume of $CHCl_3$, was spotted on 13 glass plates (10×20 cm), which were covered with alumina (thickness 0.25 mm) and the

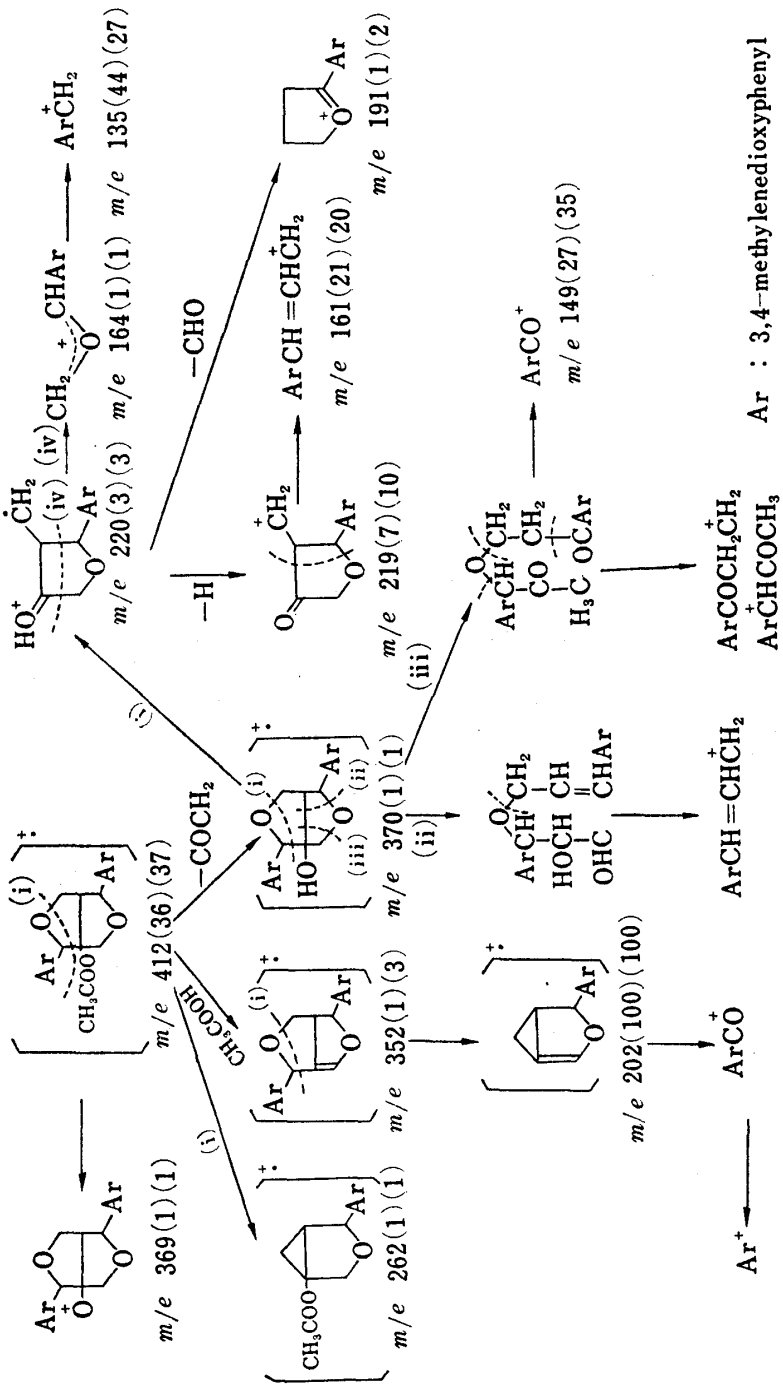


Chart 2. The Fragmentations of Paulowninacetate (VIII) and Isopaulowninacetate (XI)

Figure in the first blacket stands for the intensity of the ion from VIII and in the second blacket the intensity of the corresponding ion from XI.

plates were developed with benzene–ethyl acetate (2:1, V/V). After half drying in the air, the plate showed three bands under UV illumination, of which the middle band (Rf=0.35—0.45) was removed off and extracted with $CHCl_3$ and the $CHCl_3$ solution was evaporated to give white crystal. It was recrystallised from CH_3OH to give dihydrosesamin (II) $C_{20}H_{20}O_6$, mp 98—99°. Yield 150 mg. Rf=0.50 (benzene:ethyl acetate=4:1, V/V, silicagel). *Anal.* Calcd. for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66. Found: C, 67.15; H, 5.60. $[\alpha]_D$=20.5° (c=1.025, $CHCl_3$). From the lower band (Rf=0.22—0.17), tetrahydrosesamin[8] $C_{20}H_{22}O_6$ mp 103—104° was obtained. Rf=0.31 (benzene:ethyl acetate=4:1, V/V, silicagel). *Anal.* Calcd. for $C_{20}H_{22}O_6$: C, 67.02; H, 6.19. Found: C, 66.78; H, 6.04. From the upper band (Rf=0.80—0.93), *d*-sesamin was recovered.

Dihydrosesamin Acetate (III)——A mixture of 0.15 g of II, pyridine (5 ml) and acetic anhydride (2.5 ml) was warmed on a water bath for 50 min and after cooling, the mixture was poured into ice water. After standing in a refrigerator overnight, precipitates were filtered, dried and recrystallised from CH_3OH to give dihydrosesamin acetate (III) of mp 91—93° as colorless crystals. Yield 100 mg. Rf=0.69 (benzene: ethylacetate=4:1, V/V, silicagel). *Anal.* Calcd. for $C_{22}H_{22}O_7$: C, 66.66; H, 5.58. Found: C, 66.32; H, 5.57.

Table VI

	VIII				XI
m/e	Formula	Millimass Obsd.	Calcd.	Intensity	Intensity
412	$C_{22}H_{20}O_8$	.118	.116	36	37
369	$C_{20}H_{17}O_7$	.097	.097	1	1
352	$C_{20}H_{16}O_6$	.097	.095	1	3
262	$C_{14}H_{14}O_5$	.082	.084	1	1
219	$C_{12}H_{11}O_4$	.067	.066	7	10
202	$C_{12}H_{10}O_3$	.063	.063	100	100
161	$C_{10}H_9O_2$	.061	.060	21	20
149	$C_8H_5O_3$	.023	.024	27	35
135	$C_8H_7O_2$	.045	.045	44	27
131	C_9H_7O	.047	.050	37	30
121	$C_7H_5O_2$	.030	.029	4	5

Sodium-Liquid Ammonia Reduction of Paulownin (I)——I (1.35 g) in pure tetrahydrofuran (18 ml) was added to liquid ammonia (100 ml) at −30° (dryice–acetone) and the stirred solution was treated with sodium (190 mg). After disappearance of green color (2 hr), water (20 ml) was added to the yellow solution and ammonia was evaporated. The residue was treated with water (100 ml) and the mixture was extracted with $CHCl_3$ (3×70 ml). The $CHCl_3$ extract was distilled off to give brown oily substance, which was purified by the TLC (dry method) as in the case of II. The oily substance, dissolved in a minimum volume of $CHCl_3$, was spotted on 10 glass plates (20×20 cm) which were covered with alumina (thickness 0.25 mm) and the plates were developed with benzene–ethyl acetate (4:3, V/V). After drying in the air, the plate showed three bands under UV illumination, of which the middle band (Rf=0.47—0.67) was removed off and extracted with $CHCl_3$ and the $CHCl_3$ solution was distilled off to give dihydropaulownin (VI) of mp 125° (from EtOH). $[\alpha]_D$=−9.2° (c=0.974, $CHCl_3$). Yield 240 mg. *Anal.* Calcd. for $C_{20}H_{20}O_7$: C, 64.51; H, 5.41. Found: C, 64.35; H, 5.42. Rf=0.40 (benzene:ethyl acetate=5:2, V/V silicagel). From the lower band (Rf=*ca.* 0.24) tetrahydropaulownin (V) of mp 166—167° was obtained (from EtOH). Rf=0.23 (benzene:ethyl acetate=5:2, V/V, silicagel). *Anal.* Cacld. for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92. Found: C, 64.17; H, 6.39. Yield 10 mg. From the upper band, paulownin was recovered.

Catalytic Hydrogenolysis of Paulownin (I) with Palladium-Charcoal——A solution of 0.5 g of I and Pd-C (prepared from 5 ml of 1% palladium chloride and 0.1 g of carbon) in EtOH and tetrahydrofuran (20 ml and 20 ml) was shaken in H_2 stream. After absorption of 41 ml of H_2, the solvent was distilled off to give white crystals, which were separated into dihydropaulownin (VI) of mp 123—125° (Yield 150 mg) and tetrahydropaulownin (V) of mp 166—166.5° (Yield 30 mg) by the TLC (dry method) as mentioned above. These substances were undepressed by admixture with authentic samples.

Dihydropaulowninacetate (VII)——A solution of VI (800 mg), acetic anhydride (6 ml) and pyridine (14 ml) was warmed on a water bath for 10 min and treated as usual to give VII of mp 105—106° (from EtOH). Rf=0.50(benzene:ethyl acetate=5:2, V/V, silicagel). *Anal.* Calcd. for $C_{24}H_{22}O_8$: C, 63.76; H, 5.35. Found: C, 63.70; H, 5.64.

Sodium-Liquid Ammonia Reduction of Isopaulownin (X)——X (900 mg) in pure tetrahydrofuran (20 ml) was added to liquid ammonia (100 ml) at −30° and the stirred solution was treated as the reduction of I. The oily product was purified by the TLC (dry method, alumina as absorbant and benzene–ethyl acetate (5:1, V/V) as developping solvent). The chromatogram, after drying in the air, showed four bands under UV illumination, of which the highest band gave X and the higher band gave dihydropaulownin (VI) of mp 121—123° (from EtOH), which was undepressed by admixture with authentic sample from I. Yield 50 mg. Rf=0.37 (benzene:ethyl acetate=5:2, V/V, silicagel). *Anal.* Calcd. for $C_{20}H_{20}O_7$: C, 64.51; H, 5.41. Found: C, 64.33; H, 5.38. The lowest band gave V of mp 165—167° (mixed melting determination). Rf=0.22 (benzene:ethyl acetate=5:2, V/V, silicagel). The lower band gave oily substance which did not crystallise.

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