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LIMONOIDS FROM MELIA AZEDARACH LINN. VAR. JAPONICA MAKINO. III.[1] THE STRUCTURES OF OHCHINAL AND OHCHININ ACETATE

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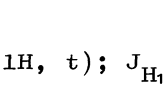
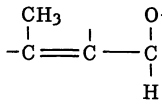
Two new limonoids, ohchinal and ohchinin acetate, have been isolated from the fruit of M. azedarach Linn. var. japonica Makino and their structures established as 1 and 2 on the basis of chemical and spectroscopic evidence.

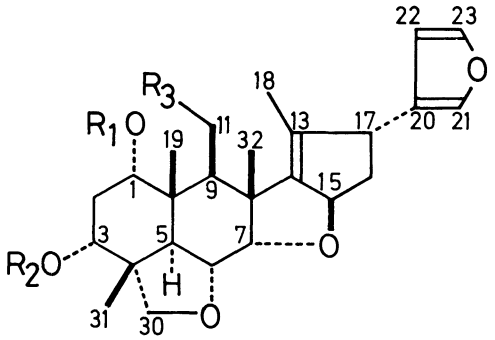
In the previous paper,[2] we reported on the structure of sendanin, a limonoid isolated from M. azedarach Linn. var. japonica Makino ("Sendan" or "Ohchi" in Japanese). In the continuation of this work, we have isolated two new limonoids, designated as ohchinal and ohchinin, the latter as its acetate, together with deacetylsalannin (3).[3] The present paper concerns with the structures of these new limonoids.

Ohchinal (1) was isolated in a 0.001 % yield as colorless prisms, $C_{35}H_{40}O_8$, mp 265-270°C, $[\alpha]_D^{27}$ +107° (c 0.10, $CHCl_3$), from the methanol extract of the fruit of M. azedarach Linn. var. japonica Makino by solvent partitions and careful silica gel column chromatography, and exhibits the following spectral data. IR (KBr): 3150, 3080, 2740, 1740, 1725, 1700, 1605, 1510, and 870 cm^{-1}; UV (EtOH): 225, 275, and 282 nm (ε 14800, 1880, and 1820); ^1H NMR: Table 1; ^{13}C NMR: Table 2. These data suggest that (1) has a β-substituted furan ring, a formyl group, an acetoxyl group, and a benzoyloxyl group. In addition, the NMR signal due to the formyl proton is transformed from a broad doublet to a doublet of doublets with the rise of temperature[4] and this fact indicates that the formyl group is contiguous to a methylene group and is sterically crowded. The ^1H NMDR studies also show the presence of following groupings.  [H_1: δ 5.05 (1H, t), H_2: δ 2.35 (2H, t), and H_3: δ 5.02 (1H, t); $J_{H_1,H_2}=J_{H_2,H_3}=3$ Hz],  [H_5: δ 2.97 (1H, d), H_6: δ 4.04 (1H, dd), and H_7: δ 4.23 (1H, d); $J_{H_5,H_6}=12$ Hz and $J_{H_6,H_7}=3$ Hz], and  [δ 1.55 (3H, d) and 5.33 (1H, m); $J_{homoallylic}=2$ Hz].

These evidence and the scrutiny of ^{13}C NMR data suggest close structural relationship between (1) and salannin (4),[3] which is verified by chemical

correlation of (1') with deacetylsalannin (3). Thus, the alkaline hydrolysis of (1), followed by sodium borohydride reduction, gave a triol (5) which was found to be identical with the compound derived from (3) via the diol (6).[3]

The location of the acetoxyl and benzoyloxyl groups is deduced from the inspection of ^{1}H NMR data. Namely, the signals due to the formyl proton in (1) and the ester methyl group in (7), which has been derived from (1) by the oxidation with Jones reagent, followed by treatment with CH_2N_2, appear at abnormally high fields (δ 8.88 and 2.86 respectively). These observations would be reasonably interpreted through the consideration of the diamagnetic anisotropy by the benzoyloxyl group present at C-1. The resonance due to the acetate methyl in (1) also appears at a rather shielded position (δ 1.79) and this fact would be easily understandable provided that the acetoxyl group present at C-3α is in a 1,3-diaxial relationship to the C-1α benzoyloxyl group. The conversion of the formyl group to a hydroxymethyl group does not result in substantial change in the resonance position of the acetate methyl as shown in the spectrum of (8) (δ 1.72), which has been derived from (1) by sodium borohydride reduction. Consequently, ohchinal must be represented by structure 1. The structure of ohchinal is interesting from the biogenetic point of view since it represents the initial product derived from 14,15-epoxy-12-hydroxy precursor.[5,6]



1 $R_1 = CO{\cdot}Ph$, $R_2 = Ac$, $R_3 = CHO$

2 $R_1 = Cin$, $R_2 = Ac$, $R_3 = CO_2Me$

3 $R_1 = Tig$, $R_2 = H$, $R_3 = CO_2Me$

4 $R_1 = Tig$, $R_2 = Ac$, $R_3 = CO_2Me$

5 $R_1 = R_2 = H$, $R_3 = CH_2OH$

6 $R_1 = R_2 = H$, $R_3 = CO_2Me$

7 $R_1 = CO{\cdot}Ph$, $R_2 = Ac$, $R_3 = CO_2Me$

8 $R_1 = CO{\cdot}Ph$, $R_2 = Ac$, $R_3 = CH_2OH$

9 $R_1 = Cin$, $R_2 = H$, $R_3 = CO_2Me$

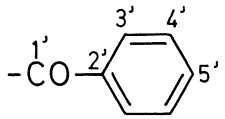
Table 1. ^{1}H NMR spectra of (1) and (2) (solvent $CDCl_3$, δ values)[a,b]

	(1)		(2)	
H-1	5.05 t	J=3	4.87 t	J=3
H-2	2.35 t	J=3	ca. 2.31	
H-3	5.02 t	J=3	5.01 t	J=3
H-5	2.97 d	J=12	2.93 d	J=12
H-6	4.04 dd	J=12, 3	4.05 dd	J=12, 3
H-7	4.23 d	J=3	4.25 d	J=3
H-12	8.88 br d (dd	J=4 J=4, 1.5)[c]		
H-15	5.33 m		5.57 m	
H-18	1.55 d	J=2	1.70 d	J=2
H-30	3.64, 3.81 AB q	J=8	3.63, 3.79 AB q	J=8
Furan	5.78, 6.99, 7.16		6.23, 7.16, 7.18	
C-Me	1.05, 1.29 (x2)		1.03, 1.26, 1.34	
CO_2Me			3.21	
OAc	1.79		1.95	
H-2'			6.47 d	J=16
H-3'			7.80 d	J=16

a) Coupling constants are expressed in Hz.

b) Recorded at 25°C.

c) Observed at 60°C.



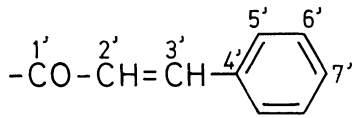


Table 2. ^{13}C NMR spectra of (1) and (2) (solvent $CDCl_3$, δ_C values, TMS as standard)[7]

Carbon atom	(1)	(2)
1*	72.1 d	71.7 d
2	28.2 t	27.7 t
3*	72.7 d	72.6 d
4	42.9 s	42.7 s
5	40.2 d	39.9 d
6	71.3 d	71.3 d
7	85.8 d	85.8 d
8	48.7 s	49.1 s
9	38.3 d	39.5 d
10	40.9 s	40.7 s
11	40.7 t	30.7 t
12	199.1 d	172.6 s
13	136.9 s	134.9 s
14	145.1 s	146.4 s
15	88.1 d	88.0 d
16	41.8 t	41.3 t
17	49.7 d	49.4 d
18	15.4 q	15.2 q
19	16.9 q	16.9 q
20	126.6 s	126.9 s
21	138.3 d	138.6 d
22	109.7 d	110.4 d
23	143.2 d	142.8 d
30	77.9 t	77.6 t
31	19.7 q	19.6 q
32	13.4 q	13.0 q
$CO_2\underline{C}H_3$		51.5 q
$OCO\underline{C}H_3$	21.0 q	21.1 q
$O\underline{C}OCH_3$	170.4 s	170.3 s
Other	[OCOPh]	[OCOCH=CHPh]
	C-1' 165.0 s	C-1' 165.4 s
	2' 129.7 s	2' 118.7 d
	3' 129.7 d	3' 144.6 d
	4' 128.7 d	4' 134.3 s
	5' 133.7 d	5' 127.9 d
		6' 129.0 d
		7' 130.3 d

* These rows may be interchanged.

Ohchinin acetate (2) was isolated in a 0.002 % yield as colorless prisms, $C_{38}H_{44}O_9$, mp 223-226°C, $[\alpha]_D^{23}$ +227° (c 0.23, EtOH), by the acetylation of the more polar fractions and displays the spectral data similar to those of ohchinal (1) and salannin (4). IR (KBr): 3160, 3060, 1735, 1715, 1695, 1640, 1585, 1500, and 875 cm^{-1}; UV (EtOH): 279 nm (ε 21800); ^1H NMR: Table 1; ^{13}C NMR: Table 2. This fact suggests that (2) also has a structure close to that of salannin (4), in which the tigloyloxyl group of (4) is displaced by a cinnamoyloxyl group. This was confirmed by the conversion of (2) into the diol (6). The alkaline hydrolysis of (2) and subsequent treatment with CH_2N_2 gave methyl cinnamate and (6), which was also obtained from (3) in the same way. The cinnamoyloxyl group must be attached at C-1 and the acetoxyl group at C-3, rather than the reverse, for the following reason. In the ^1H NMR spectrum of (2), the signal due to the ester methyl group is observed at an unusually high field (δ 3.21) as in the case of salannin (4).[3] It could be assumed quite reasonably that a cinnamoyloxyl group exerts a shielding effect of the same degree as a tigloyloxyl group to the protons which are disposed over the ethylenic linkage. Thus, structure 2 is assigned to ohchinin acetate.

The natural precursor of (2) should be (9), for which the name ohchinin is reserved, although we have not yet succeeded in its isolation.

References and Notes

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2) M. Ochi, H. Kotsuki, K. Hirotsu, and T. Tokoroyama, Tetrahedron Lett., 1976, 2877.

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4) V. P. Gullo, I. Miura, K. Nakanishi, A. F. Cameron, J. D. Connolly, F. D. Duncanson, A. E. Harding, R. McCrindle, and D. A. H. Taylor, J. Chem. Soc. Chem. Commun., 1975, 345.

5) Actually we have isolated a limonoid closely related to this precursor from M. azedarach Linn. var. japonica Makino and will publish shortly on its structural work.

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7) We thank Professor K. Nakanishi, Columbia University, for the ^{13}C NMR data of salannin.

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