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TRICHILININ, A NEW HEXACYCLIC LIMONOID FROM *TRICHILIA ROKA*

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Abstract - A new limonoid, trichilinin, has been isolated from the root bark of *Trichilia roka* and its structure established by NMR and CD studies. It appears to be a biogenetic precursor of salannin.

Previously[1], we have reported on the structures of potent insect antifeedants, trichilins, from the root bark of East African medicinal plant *T. roka* (Meliaceae). In continuous work, we now isolated a new limonoid belonging to vilasinin class[2] as a minor component. The present paper concerns with the structure of this limonoid designated as trichilinin.

Final purification by HPLC after extensive chromatography of the ether extract of the root bark (365 g) afforded 9 mg of trichilinin (1), $C_{30}H_{40}O_8$, which exhibited the following spectral data. EI-MS: 528(M^+), 468(M^+-60), 453, 357; UV: 210 nm(ε 3700); IR: 3300-3600 cm^{-1}. From the ^1H NMR (360 MHz, $CDCl_3$) data, four tertiary methyl groups at δ 0.94(s, 10-Me), 1.12(s, 8-Me), 1.12(s, 13-Me) and 1.19(s, 4β-Me) were observed along with two acetoxyl methyls at 1.91 and 2.13, a trisubstituted

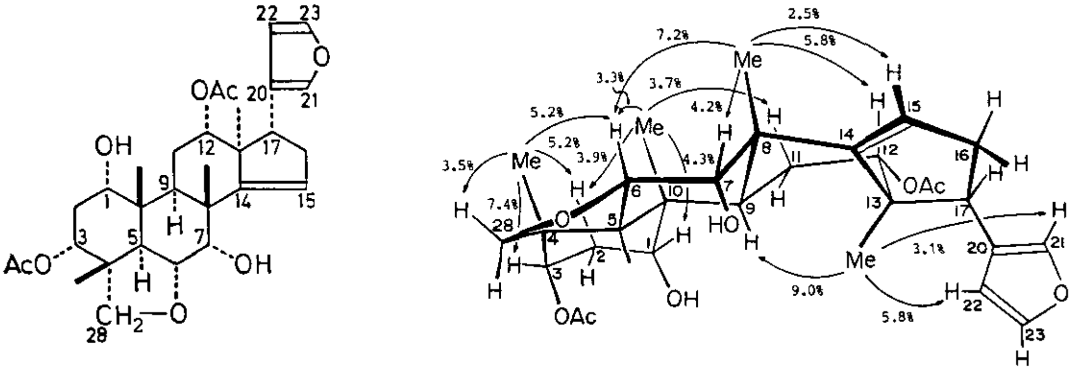

Fig. 1. Trichilinin (1), structure and NOE's between methyl and proton.

olefinic proton at 5.70(dd, J= 3 and 1.5, 15-H), and a specific AB quartet at 3.59 (J= 7.5, 28β-H) and 3.45(br, J= 7.5, 28α-H), weakly coupled to 4β-Me. Two methine protons under hydroxyl group at 3.45(br, 1-H) and 4.21(d, J= 3, 7-H), coupling with a methine proton at 4.16(dd, J= 12 and 3, 6-H) linked to an ether oxygen, were also observed along with two protons under two acetoxyl groups at 5.09(dd, J= 3 and 2.5, 3-H) and 5.07(dd, *J= 9* and 7, *12-H*). *A characteristic double doublet due to 17β-H* at 3.04(J= 11 and 8) showed further weak coupling with furan protons at 7.23(21-H) and 7.35(23-H)[1b]. Decoupling study of the spectrum allowed us to assign all coupled protons (Table 1). These assignments were comfirmed with NOE measurements (4β-Me/2β-H, 3β-H and 6β-H; 8-Me/6β-H, 7β-H, 12β-H and 15-H; 10-Me/1β-H, 2β-H, 6β-H and 11β-H; 13-Me/9-H, 21-H and 22-H), which revealed the gross comformation (Fig. 1). In particular, the location of the 12-acetoxyl group was comfirmed by the NOE(5.8%) between the 8-Me and 12-H. The structure **1** was further supported by the ^{13}C NMR spectrum (25 MHz, $CDCl_3$: Table 1); the assignments are based on the comparison with the data of the known related limonoids[3-6].

The relationship between the furan, double bond and 7-hydroxyl group was also derived from the CD spectra of **1** and the benzoate **2**. In the CD of **1** (Fig. 2), the

Table 1. ^{13}C and ^{1}H NMR Data of Trichilinin (1)

C	δ	Mult	H	δ	Mult	J/Hz	coupled to	C	δ	Mult	H	δ	Mult	J/Hz	coupled to
1	71.8	d	1	3.45	br		2α,2β,OH	16	36.8	t	16α	2.58	ddd	16,11,1.5	16β,17,15
2	30.1	t	2α	1.98	dt	16.5,2.5	2β,1,3				16β	2.47	ddd	16,8,3	16α,17,15
			2β	2.30	dt	16.5,3	2α,1,3	17	50.3	d	17	3.04	dd	11,8	16α,16β
3	74.0	d	3	5.09	dd	3,2.5	2β,2α	18	27.1	q	18	1.12	s		
4	42.5	s						19	15.5	q	19	0.94	s		
5	38.9	d	5	2.42	d	12	6	20	124.6	s					
6	72.5	d	6	4.16	dd	12,3	5,7	21	140.2	d	21	7.23	dd	1.5,1.2	23,22
7	78.0	d	7	4.21	d	3	6	22	111.8	d	22	6.28	dd	2,1.2	23,21
8	45.3	s						23	142.0	d	23	7.35	dd	2,1.5	22,21
9	34.8	d	9	2.88	dd	17,8	11β,11α	28	73.6	t	28α	3.45	brd	7.5	28β,29
10	40.2	s									28β	3.59	d	7.5	28α
11	36.8	t	11α	1.49	m		9,11β,12	29	19.1	q	29	1.19	brs		
			11β	2.18	m		9,11α,12	30	15.6	q	30	1.12	s		
12	77.8	d	12	5.07	dd	9,7	11β,11α	2x OAc	21.3	q	Ac	1.91	s		
13	51.7	s							169.6	s					
14	157.6	s							21.2	q	Ac	2.13	s		
15	122.6	d	15	5.70	dd	3,1.5	16β,16α		171.0	s					

^{13}C and ^{1}H NMR spectra were recorded in $CDCl_3$ at 25 and 360 MHz, respectively.

positive Cotton effect at 221 nm is one of the two extreme of a split CD, which could be arized from the positively coupled oscillator of the furan and double bond. In the spectrum of 1,7-dibenzoate **2**, a CD curve with negative/positive Cotton effects at 238 nm/220 nm was observed. In view of the additivity relation on interactions between different chromophores[7], the Δ_ε= +4.3 value is a summation of two interactions of furan /double bond and 7-OBz/furan (negative)[8], arizing from negatively coupled oscillator; interactions of 1-OBz/ 7-OBz (dihedral angle is ca 0°) and 7-OBz/double bond are negligible.

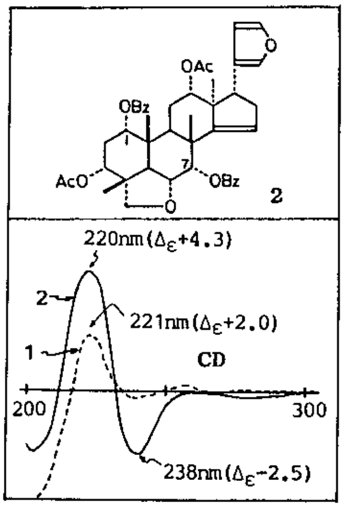

Fig. 2. CD spectra of **1** and **2**.

Although there have been reported some meliacans being engaged in an ether linkage at C_{28}-C_6[2,9,10], the C-12 oxygen function as in **1** is at present unique. Trichilinin could be biogenetically derived from sendanal (28-CHO)[4] and also a precursor of salannin type limonoids[11] in which ring C was cleaved.

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REFERENCES AND NOTES

1. a) M. Nakatani, J. C. James, and K. Nakanishi, J. Am. Chem. Soc., 1981, **103**, 1228. b) M. Nakatani, I. Iwashita, H. Naoki, and T. Hase, Phytochemistry, 1985, **24**, 195.
2. P. V. Pachapurkar and P. M. Kornule, Chem. Lett., **1974**, 357.
3. M. Ochi, H. Kotsuki, T. Kataoka, T. Tada, and T. Tokoroyama, Chem. Lett., **1978**, 331.
4. M. Ochi and H. Kotsuki, Chem. Lett., **1978**, 621.
5. S. Siddiqui, B. S. Siddiqui, S. Faizi, and T. Mahmood, Phytochemistry, **1984**, **23**, 2899.

6. H. S. Garg and D. S. Bhakuni, Phytochemistry, 1985, **24**, 866.
7. R. S. Stonard, D. A. Trainor, M. Nakatani, and K. Nakanishi, J. Am. Chem. Soc., 1983, **105**, 130.
8. 7-OBz/furan of trichilin B 7-benzoate: 242 nm(Δ_{ε} -3.2)/217 nm(Δ_{ε} +7.2).
9. D. E. U. Ekong, C. O. Fakunle, A. K. Fasina, and J. I. Okogun, Chem. Commun., **1969**, 1166.
10. K. K. Purushothaman, K. Duraiswamy, and J. Connolly, Phytochemistry, 1984, **23**, 135.
11. R. Henderson, R. McCrindle, A. Melera, and K. H. Overton, Tetrahedron, 1968, **24**, 1525.

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