CHEMISTRY LETTERS, pp. 1337-1338, 1986.

Stereochemistry of Merolimonol by ^{1}H NMR and CD Spectral Studies

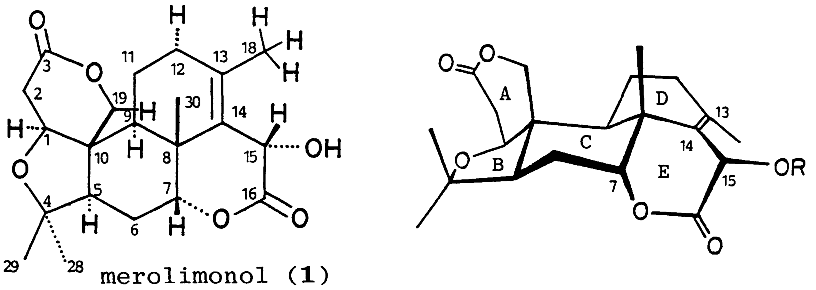
Munehiro NAKATANI, Takashi IWASHITA,† Hideo NAOKI,† and Tsunao HASE
Faculty of Science, Kagoshima University, Kagoshima 890
†Suntory Institute for Bioorganic Research, Shimamotocho, Mishimagun, Osaka 618

The stereochemistry of merolimonol was investigated by ^{1}H NMR study including COSY and NOESY, and CD application to the benzoates confirmed the ring conformation.

Merolimonol (**1**) has been derived from limonin *via* limonol and the structure assumed from the reaction mechanism.$^{1,2)}$ But, there is no chemical and spectral assignment on the stereochemistry and so we have devoted considerable attention to it, particularly to the configuration of the C-15 hydroxyl group. We now report the stereochemistry of **1** based on ^{1}H NMR study including COSY and NOESY spectra, and CD application to the conformational study on the D- and E-rings.

Merolimonol (**1**), $C_{21}H_{28}O_6$, mp 297-300 °C(d), exhibited the following fragments in its SI-MS: m/z 377(M+1), 359(377-H_2O), 277, 233, 201, 185(base peak). From the ^{1}H NMR(360 MHz, $CDCl_3$) data, four methyl groups at δ1.05(s, 8-Me), 1.14(s, 4β-Me), 1.28(s, 4α-Me) and 1.92(br s, 13-Me) were observed, along with a specific allyl proton under a hydroxyl group at δ5.12(br s, 15-H) showing homoallylic couplings to the 13-Me signal and a signal at δ2.2(12α-H), the presence of which suggested the β orientation of the 15-H. A methine proton linked to an ether oxigen at δ4.03 (m, 1-H), coupled to methylene protons at δ2.66(dd, J=17 and 2, 2β-H) and 2.94(dd, J=17 and 3.5, 2α-H), showed a W-type long-range coupling with one part(H_b) of an AB quartet(J_{AB}=13) at δ4.32(19-H_a) and 4.47(19-H_b). 2D homonuclear J-correlation (COSY) indicated another coupling protons (Table 1) on the linked carbons(C-5, 6, 7 and C-9, 11, 12). These assignments were confirmed with cross-relaxation correlated 2D-^{1}H NMR(NOESY) of **1** (4α-Me/1-H, 5-H, 4β-Me/19-H_b, 8-Me/7-H, 15-H, 19-H_a, 19-H_b, and 9-H/1-H, 5-H), which also revealed the gross conformation (Fig. 1). The NOE (4.9%) between the 8-Me and 15-H also confirmed the α location of the 15-OH group.

The conformation of the D- and E-rings was independently derived from an



merolimonol (**1**)

1a: R= H
2 : R= Bz
3 : R= Bz-*p*-Br
4 : R= Bz-*p*-Me
5 : R= α-naphthoyl

Fig. 1.

Table 1. ^{1}H NMR Data of Compounds **1** and **2**

	Compound 1					Compound 2				
H	δ	Mult	J/Hz	coupled to [a]	NOE/% [b]	δ	Mult	J/Hz	coupled to [a]	NOE/% [b]
1	4.03	m		2a,2b,19b	9	4.06	m		2a,2b,19b	9
5	2.24	dd	13,3.5	6α,6β	9,28	2.30	dd	13,3.5	6α,6β	9,28
7	4.47	brt	3	6α,6β	30	4.66	m		6α,6β	30
9	1.83	dd	13,3.5	11α,11β	1,5	1.92	m		11α,11β	1(5.5),5(9.5)
15	5.12	brs		12α,18	30	6.37	brs		12α,18	30
18	1.92	brs		15		1.89	brs		15	2',6'(6.9)
19a	4.32	d	13	19b	30	4.34	d	13	19b	30
19b	4.47	brd	13	1,19a	29,30	4.51	brd	13	1,19a	29,30
28	1.28	s			5(9.1)	1.30	s			5(10)
29	1.14	s			19b(5.9)	1.17	s			19b(5.5)
30	1.06	s			7(5.3),15(4.9) 19a(3.4),19b(4.6)	1.17	s			7(3.4),15(5.4) 19a(5.6),19b(8.9)

a) Distinguished coupling are listed. *b)* Numerals outside parentheses denote the proton exhibiting the NOE; e.g., in the fourth line, irradiation of 9-H causes 5.5% and 9.5% NOE on 1-H and 5-H, respectively. No indication in parentheses based on 2D-NOE.

application of the new CD method for determining the absolute stereochemistry of allylic alcohols reported by Harada and Nakanishi *et al.*[3,4] Three benzoates, **2**-**4**, and a naphthoate **5**, prepared from **1** in the usual way, exhibited split CD spectra. The UV and CD spectra of the benzoate **2** are shown in Fig. 2. In the region of the benzoate π-π* trandition around 230 nm, the CD spectrum exhibits a positive Cotton effect, the sign of which should be in accordance with the positive chirality between the benzoate and double-bond chromophores. No conformation change in the benzoylation reaction was confirmed by the ^{1}H NMR measurement (Table 1). Other benzoates, **3** and **4**, and α-naphthoate **5** also showed positive chiralities on their CD spectra (Table 2). These results and Dreiding model inspection led us to determine the boat(D-) and quasi boat(E-ring) conformations.

We are grateful to Professor Koji Nakanishi, Columbia University, for his kind discussion and suggestions.

Table 2. UV and CD data of **2**-**5**

Compd	UV λ_{max}/nm(ε)	CD λ_{ext}/nm(Δε)
2	230(9800)	234(+1.8)
3	247(13000)	240(+3.1)
4	241(13200)	238(+2.2)
5	238(51000)	238(+6.4)

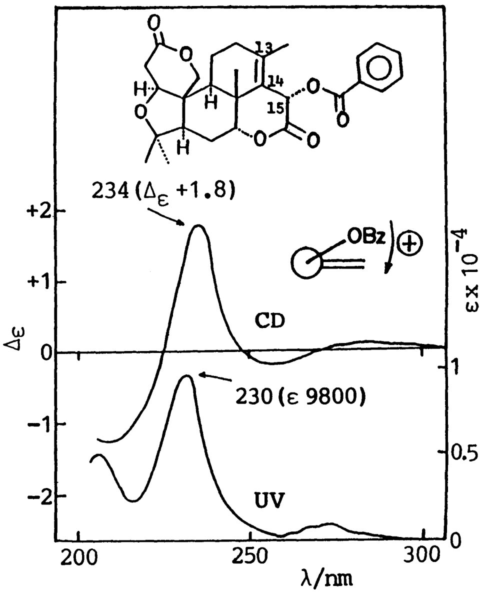


Fig. 2. UV and CD spectra of **2**.

References

1) A. Melera, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, 40, 1420 (1957).
2) D. Arigoni, D.H.R. Barton, E.J. Corey, O. Jeger, L. Coglioti, S.G. Ferrini, E.R. Glazier, A. Melera, S.K. Pradhan, K. Schaffner, S. Stemhell, J.E. Templeton, and S. Tobinaga, *Experientia*, 16, 41(1960).
3) N. Harada, J. Iwabuchi, Y. Yokota, H. Uda, and K. Nakanishi, *J. Am. Chem. Soc.*, 103, 5590(1981).
4) N. Harada and K. Nakanishi, "*Circular Dichroic Spectroscopy-Exciton Coupling in Organic Stereochemistry* (Japanese)," Tokyo Kagaku Dojin, Tokyo(1982).

(Received May 23, 1986)