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Tripterregeline A,B and C, Sesquiterpene Alkaloids from *Tripterygium regelii*

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Abstract □ Three new sesquiterpene alkaloids, tripterregeline, A,B and C were isolated from the stem bark of *Tripterygium regelii* and their partial structures were determined by various spectroscopic methods.

Keywords □ *Tripterygium regelii,* Celastraceae, alkaloid, tripterregeline, sesquiterpene, two-dimensional NMR.

Many sesquiterpene type alkaloids have been isolated from a number of Celastraceae plants[1-3] and they attracted our interest due to the potent insecticidal activity reported[4]. Present paper describes the isolation and structures of the three new sesquiterpene alkaloids from *Tripterygium regelii* (Celastraceae), tripterregeline A(1), B(2) and C(3).

From the mass and NMR (^{1}H-NMR, ^{13}C-NMR, Attached Proton Test, ^{1}H-^{1}H COSY and ^{1}H-^{13}C COSY) spectra in comparison with triptofordinine A-1[5], we could know that these alkaloids have acetyl, nicotinoyl and benzoyl group in the dihydroagarofuran type sesquiterpene skeleton. The structures of **1**, **2** and **3** are postulated as shown in Fig. 1.

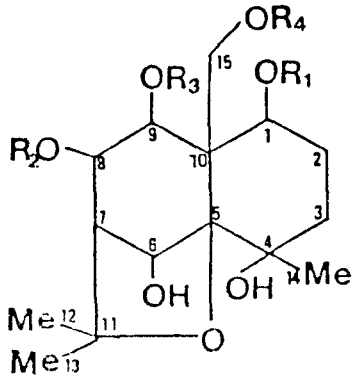

Fig. 1. Structures of tripterregeline A(1), B(2) and C(3).

Compounds	R_1*	R_2	R_3*	R_4
1	nicotinoyl	H	COPh	H
2	COPh	H	nicotinoyl	H
3	COPh	Ac	nicotinoyl	Ac

*Exchangeable between R_1 and R_3.

EXPERIMENTAL METHODS

The stem bark of *Tripterygium regelii* collected in July, 1987 at Mt. Dukyoo, Korea was powdered and extracted with MeOH (20 L) and concentrated to give a MeOH Ex.(800g). By conventional method, Et_2O soluble alkaloidal fraction (6.5g) was obtained from MeOH extract. The alkaloidal fraction was chromatographed on silica gel developed successively with $CHCl_3$/MeOH (40:1→ 1:1) to yield fr.1 (0.94g), fr.2 (0.86g), fr.3(1.54g), fr.4(0.90 g), fr.5(0.64g), fr.6(0.44g) and fr.7(0.18g).

1. Tripterregeline A and B

Fr. 3 was chromatographed on alumina (neutral) and rechromatogaphed on silica gel with EtOAc/MeOH(50:1) to yield two colorles needle crystals, tripterregeline A(18mg) and B(23mg).

Tripterregelin A(1): $C_{28}H_{33}NO_9$, mp 224 °. UV λ_{max} (EtOH) nm (ε): 224(13500), 265(2300). ^{1}H-NMR (CD_3OD, 300 MHz): Table I. ^{13}C-NMR(CD_3OD, 75.5 MHz): Table II. SIMS, *m/z*: 528 $[M+M]^+$, 550 $[M+NA]^+$.

Tripterregeline B(2): $C_{28}H_{33}NO_9$. mp 190 °. UV λ_{max} (EtOH) nm(ε): 224 (11200), 266 (1900). ^{1}H-NMR ($CDCl_3 + CD_3OD$, 300 MHz): Table I. ^{13}C-NMR ($CDCl_3 + CD_3OD$, 75.5 MHz): Table II. EIMS, *m/z*, (Rel. Int. %): 527 (M^+, 0.5), 124 (100.0), 105 (94.0).

Table I. ^{1}H-NMR data of tripterregeline A(1), B(2) and C(3)

No. of proton	1 ppm	2 ppm	3 ppm
H-1	5.72 dd	5.62 dd	5.68 dd
	(12.2, 4.4)	(12.2, 4.4)	(10.5, 5.9)
H-2_{AB}	1.65-	1.55-	1.80-
H-3_A	1.85	1.75	2.20
	m	m	m
H-3_B	2.10 ddd	1.95 ddd	
	(12.3,12.2,6.0)	(10.2,10.0,4.5)	
H-6	5.64 brs	5.38 brs	5.31 brs
H-7	2.33 d	2.33 d	2.46 d
	(4.3)	(4.1)	(4.2)
H-8	4.30 dd	4.23 dd	5.58 dd
	(5.3, 4.3)	(5.7, 4.1)	(5.2, 4.2)
H-9	5.72 d	5.68 d	5.80 d
	(5.3)	(5.7)	(5.2)
H-12	1.61 s	1.53 s	1.60 s
H-13	1.58 s	1.54 s	1.70 s
H-14	1.75 s	1.69 s	1.72 s
H-15	4.35, 4.45	4.25, 4.34	4.88, 5.04
	AB_q (12.1)	AB_q (12.1)	AB_q (13.3)
Ac	—	—	2.01 s
			2.25 s

Figures in parentheses are coupling constants in Hz, run at 300 MHz in CD_3OD(**1**), $CD_3OD + CDCl_3$(**2**) and $CDCl_3$(**3**).

2. Tripterregeline C

Fr.1 was chromatographed on silica gel with $CHCl_3$/MeOH (30:1), fr.A (110 mg), fr.B (430 mg) and fr.C (720 mg) were obtained. Fr.C was rechromatographed on silica gel with Benzene/EtOH (40:1) to give colorless needle crystals, tripterregeline C (**3**, 17 mg). $C_{32}H_{37}NO_{11}$, mp 195°. UV λ_{max} (EtOH) nm(ε): 224 (12800), 266 (2200). ^{1}H-NMR ($CDCl_3$, 300 MHz): Table I. ^{13}C-NMR ($CDCl_3$, 75.5 MHz): Table II. EIMS, *m/z*, (Rel. Int. %): 611 (M^+,7.07), 552 (M^+-CH_3COO, 15.11), 551 (M^+-CH_3COOH, 41.52), 426 (230.04), 124 (64.07), 105 (100.00), 77 (13.53).

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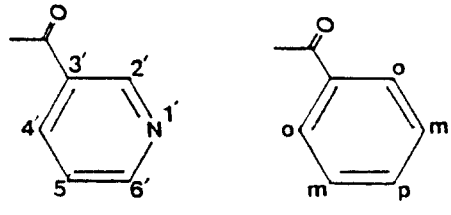
Table II. ^{13}C-NMR data of tripterregeline A(1) and B(2)

No. of carbon	1 ppm	2 ppm
C-1	79.6*	78.7*
C-2	26.2	25.9
C-3	36.3	30.4
C-4	73.6	72.9
C-5	92.7	92.6
C-6	75.1	74.4
C-7	58.5	58.4
C-8	68.8	68.2
C-9	77.7*	78.3*
C-10	55.4	55.0
C-11	83.6	82.6
C-12	24.8	24.9
C-13	30.3	30.4
C-14	25.5	25.8
C-15	59.2	58.9
2′	153.6	153.4
3′	127.3	126.3
4′	138.4	136.7
5′	124.6	123.5
6′	150.7	150.9
ortho	130.3	129.7
meta	129.4	128.3
para	134.2	133.1
ipso	130.7	130.2
CO	166.5	165.3
	165.8	164.5

Recorded at 75.5 MHz in CD_3OD(**1**), and $CD_3OD + CDCl_3$(**2**)

*Values in each column may be interchanged.



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