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Isolation and structure Determination of Peradione (1) a Novel Triterpene With a Rearranged Perovskane Skeleton From *Perovskia abrotanoides*

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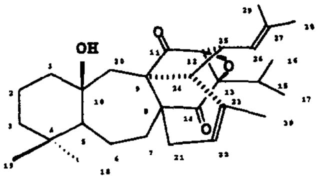
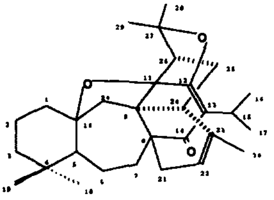
Abstract:. A novel triterpene peradione(1), has been isolated from *Perovskia aabrotanoides* a Pakistani medicinal plant. The structure of this compound was elucidated by extensive spectroscopic studies.

We have recently reported the isolation of a new triterpene perovskone (2)[2] with a novel carbon skeleton from *Pervoskia abrotanoides* Kerel (Labiatae). In this communication we wish to report the isolation and structure elucidation of another new triterpene peradione(1), possessing a anovel carbon skeleton from the hexane extract of the same plant. The whole plant material (18Kg)collected at Ziarat, Baluchistan was soaked in n-hexane (40L). After extraction peradione(1), was separated by flash chromatography on silica gel column and elution with $CHCl_3$.



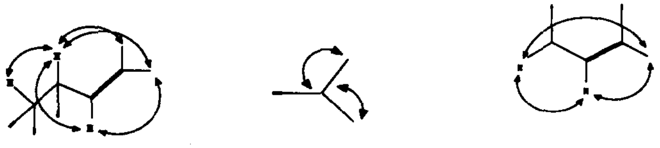
(1)



(2)

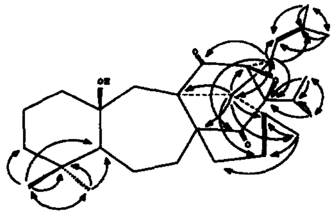
Peradione (1), colourless needles (from MeOH), $[\alpha]_D = 0$ ($CHCl_3$), m.p. 210°C, showed UV absorptions (MeOH) at 201.6, 250.0 nm and IR (KBr) bands at 3500 (OH), 1740 (CO), 1700 (CO) and 1300cm-1 (ether). The molecular formula of peradione(1), $C_{30}H_{42}O_4$ was determined by HRMS (m/z 466.3047), indicating 10 degrees of unsaturation in the molecule. The E.I. spectrum showed peaks at 466 (M^+), 451 $(M\text{-}CH3)^{+}$, 450 (M^+-oxygen, typical of epoxide), 438 (M^+-CO, typical of ketones), 423 (M-isopropyl)$^+$, 412, 411, 382, 354, 340, and 283. ^{13}C NMR (Broad Band and DEPT) experiments revealed peaks of all 30 carbon atoms attached to a total of 42 hydrogen atoms, with seven methyl, seven methylene, six methine and ten quaternary carbon atoms (Table 1.). The ^{1}H- and ^{13}C-NMR spectra of (1), indicated the presence of two ketonic groups (δC 202.4 and 210.2), two double bonds (δH 4.60 and 5.34; δC 120.1, 122.0, 133.3 and 133.4), three oxygen- bonded quaternary carbons (δC 70.1, 90.5, 100.4), five tertiary methyl groups (δH 0.84, 0.95, 1.50, 1.63 and 1.64; δC 32.6, 21.7, 18.0, 25.7 and 24.6) and two secondary methyl groups (δ H 0.79, and 1.09; δC 21.7 and 25.7).

A ^{13}C decoupled HMQC (J, 500Hz) spectrum led to the assignments of ^{1}H- and ^{13}C- NMR signals. ^{1}H-^{1}H 2D-COSY-45 and HOHAHA spectra of (1), provided sufficient information to enable the ring system and its substitution pattern to be deduced. Thus the protons of both C-16 (δH 0.79) and C-17 (δH 1.09) methyl groups are coupled to H-15 (δH 1.98). In the same way the protons of C-18 (δH 0.84) and C-19 (δH 0.95) methyl groups coupled to H-3 (δH 1.13) and H-5 (δH 1.21). The protons of C-29 (δH 1.63) and C-28 (δH 1.64) methyl groups showed coupling with H-26 (δH 4.60), H-25 (δH 3.72) which further coupled to H-24 (δH 2.72). The protons of C-30 (δH 1.50) methyl group showed allylic coupling to C-22 (δH 5.34) and both protons of C-21 (δ H 2.44, 2.50). The ^{1}H-^{1}H 2D-COSY-45, HOHAHA and ^{1}H - ^{13}C spectra of (1), suggested the presence of the partial structural units A, B and C (Fig. 3).



(A) (B) (C)

Partial Structural Units for Peradione (1), Fig. 3.



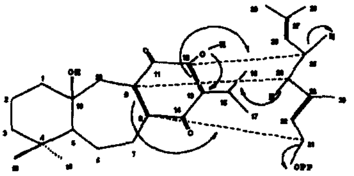
HMBC Correlations for (1), Fig. 4.

TABLE 1. NMR DATA of Peradione[a]

C#	^{13}Cδ	MULT.[b]	^{1}Hδ (mult.,J,Hz)[c]	HMBC[d]	NOESY[e]
1	40.9	CH_2	1.85(m)		
2	19.5	CH_2	1.45(m)		
3	41.2	CH_2	1.13(m)		
4	35.9	C			
5	49.8	CH	1.21(m)		
6	20.7	CH_2	1.82(m)		
7	31.0	CH_2	1.24(m)		
8	50.3	C			
9	51.3	C			
10	90.5	C			
11	210.2	C			
12	100.4	C			
13	70.1	C			
14	202.4	C			
15	25.4	CH	1.98(m)	C-16,C-17	
16	15.3	CH_3	0.79(d,J=6.9Hz)	C-13,C-15,C-17	
17	18.4	CH_3	1.09(d,J=6.9Hz)	C-13,C-15,C-16	
18	32.6	CH_3	0.84(s)	C-3,C-4,C-5,C-19	
19	21.7	CH_3	0.95(s)	C-3,C-4,C-5,C-18	
20	42.4	CH_2	1.42(m)		
21	28.6	CH_2	4.44(dd,J=18,24Hz)		
22	122.0	CH	5.34(s)		H-21,H-30
23	123.4	C			
24	43.5	CH	2.72(d,J=10Hz)	C-8,C-9,C-22,C-23, C-25,C-26,C-27,C-30	H-25,H-26
25	43.1	CH	3.72(dd,J=10,21Hz)	C-11,C-13,C-14,C-24 C-26,C-27	
26	120.1	CH	4.60(d,J=10Hz)		H-25,H-28,H-29
27	133.3	C			
28	18.0	CH_3	1.63(s)	C-26,C-27,C-29	
29	25.7	CH_3	1.64(s)	C-26,C-27,C-28	
30	24.6	CH_3	1.50(bs)	C-22,C-23,C-24	H-21,H-22

[a] All the spectra recorded in $CDCl_3$. [b] Determined by DEPT/HMQC experiments. [c] Assignments based on HMQC and 2D J Resolved results. [d] Carbon number with which the proton is correlated. [e] Correlation of protons in space.

These structural units were connected with the long range heteronuclear correlations obtained in a proton detected long range multiple quantum (HMBC)[3] experiment and the connectivities shown in (Fig. 4) can easily be deduced. The structural features around C-24 was determined by NOESY between H-25/Me-28 and 29. The connectivities of C-24/C-25 with C-12, C-13 and C-26 were further supported by the down field chemical shifts of H-24 and H-25 (δH 2.72 and 3.72) typical for methine proton adjacent to sp^2 carbon[4]. The biogenesis of (1) may be assumed to proceed from a precurser of icetexone[5] and geranyl pyrophosphate (Fig. 5.) as in perovskone but in case of peradione a C-C bond formation takes place between C-12 and C-25 instead of C-11 and C-26.



Possible Biogenetic Pathway for (1) Fig. 5.

References and Notets

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