Structure of Pilosanones A and B: Novel Diterpenoids with a Bicyclo[5.4.0]undecane Skeleton from *Portulaca pilosa* L.

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Pilosanones A (**1**) and B (**2**), the major diterpenoid constituents of *Portulaca pilosa* L., have been assigned structures with a novel bicyclo[5.4.0]undecane skeleton on the basis of detailed spectroscopic analyses, and their significance in the biosynthesis and the chemosystematics of *Portulaca* plants is suggested.

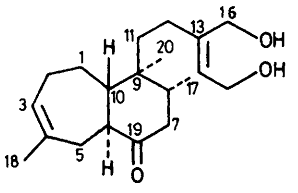
We report here the isolation and structure elucidation of pilosanones A (**1**) and B (**2**), the major constituents of *Portulaca pilosa* L., which have a novel bicyclo[5.4.0]undecane skeleton[1,2] and could be significant in relation to the biogenesis and chemosystematics of the diterpenoids[1,3—5] in *Portulaca* plants.

The aerial part (3.4 kg) of *P. pilosa* L., collected at Iriomote island and cultivated at the plant garden of Osaka City University, was extracted with methanol and the extract partitioned successively with hexane and ethyl acetate. Chromatographic separation of the ethyl acetate extract over silica gel afforded pilosanones A (0.8 g) and B (0.9 g).

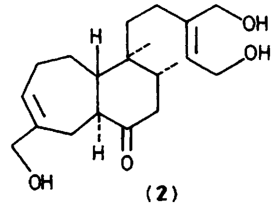
The less polar compound, pilosanone A (**1**), m.p. 98.5—99.0 °C, $[\alpha]_D^{30.5}$ −51.1° (*c* 0.56, EtOH); *m/z* 320.2329 ($C_{20}H_{32}O_3$ requires 320.2352, M^+), exhibited OH and carbonyl i.r. absorption bands at 3400 and 1710 cm^{-1}, respectively ($CHCl_3$). Inspection of the ^1H and ^{13}C n.m.r. data (Tables 1 and 2) indicated the presence of a 5-hydroxy-3-

hydroxymethylpent-3-enyl side chain, characteristic of the diterpenoids found in *Portulaca* plants, as well as a trisubstituted double bond appended with a methyl group (H-3 at δ 5.55 and H-18 at δ 1.72). Thus compound (**1**) must be bicyclic, one of the rings being six-membered, as revealed by the carbonyl i.r. absorption. The ring proton signals in the ^{1}H n.m.r. spectrum (400 MHz) were correlated by the application of 2D-COSY and homonuclear spin decoupling (HNSD) techniques with reference to the data of portulal (**3**) and poltulene (**4**).[1] Results are in Table 1. The angular protons are observed at δ 2.32 (H-6) and δ 1.72 (H-10), and the coupling constant between them (10.5 Hz) suggested *trans* ring fusion. The carbonyl group, and secondary (δ 0.91) and tertiary methyl groups (δ 0.92) are placed at C-19, C-8, and C-9, respectively. The ^{13}C n.m.r. spectrum, assigned by INEPT, ^{1}H-selective decoupling, and ^{1}H–^{13}C COSY, supported structure (**1**) for pilosanone A.

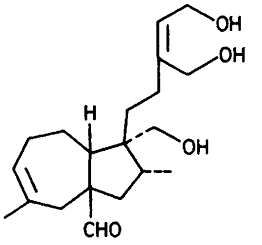
The more polar compound, pilosanone B (**2**), a colourless oil, $[\alpha]_D^{30.5}$ −52.2° (*c* 1.27, EtOH), contains one more oxygen atom than (**1**), as shown by its high resolution mass spectrum, *m/z* 336.2293 ($C_{20}H_{32}O_4$ requires 336.2300, M^+). Compound (**2**) exhibited i.r. absorption bands at 3400 (OH) and 1710 cm^{-1} (C=O). The ^{1}H and ^{13}C n.m.r. spectra of (**2**) closely resemble those of (**1**), the major difference being the observation of a methylene singlet at δ 3.93 in the ^{1}H n.m.r. spectrum instead of the vinylic methyl signal at δ 1.72 in (**1**), irradiation of the former signal sharpening the H-3 resonance. The chemical shifts of 3-H and 5-H$_\alpha$ were somewhat deshielded compared to those of (**1**). This evidence, in conjunc-



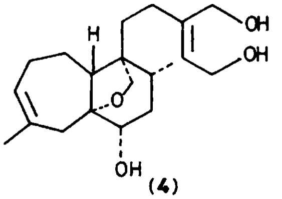
(**1**)



(**2**)



(**3**)

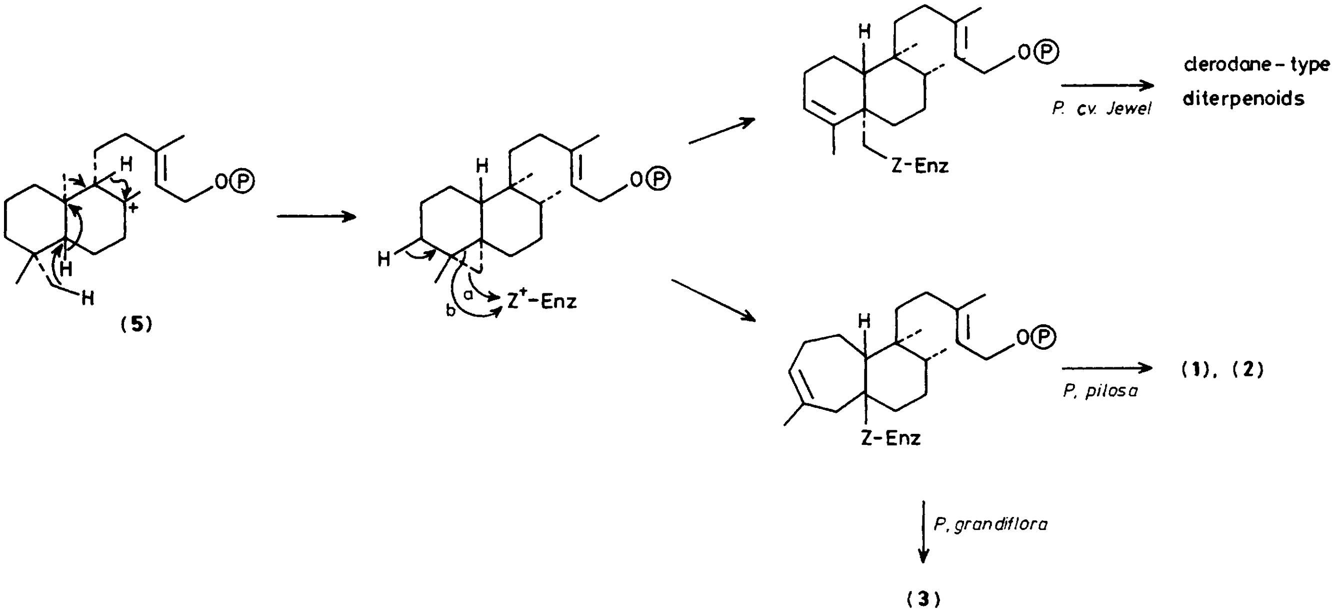


(**4**)

Table 1. ^{1}H N.m.r. data for (**1**) and (**2**) (400 MHz, $SiMe_4$).[a]

H	δ (1) ($CDCl_3$)	δ (2) (CD_3OD)
1α	1.35dddd	1.40dddd
1β	1.85m	1.95^b
2α	2.18^b	2.30br dt
2β	2.00^b	2.08^b
3	5.55br t	5.82br t
5α	2.62d	2.73dd
5β	2.12dd	2.08^b
6	2.32t	2.43ddd
7α	2.36t	2.45t
7β	2.22dd	2.16dd
8	1.95^b	1.97^b
10	1.72^b	1.77ddd
11	1.56m	1.66m
12	1.95^b	2.00^b
14	5.60t	5.48t
15	4.19d	4.13d
16	4.16s	4.11s
17	0.91d	0.95d
18	1.72br s	3.93br s
20	0.92s	0.96s

[a] *J* (1) (1α, 10) 9.3, (1α, 1β) 13.9, (1α, 2β) 11.7, (1α, 2α) 2.4, (3, 2α) = (3, 2β) = 5.6, (5α, 5β) 15.4, (5β, 6) 10.5, (6, 10) 10.5, (7α, 7β) = (7α, 8) = 13.7, (7β, 8) 3.7, (8, 17) 7.2, (14, 15) 6.8; (2) (1α, 10) 9.3, (1α, 1β) 13.9, (1α, 2β) 11.7, (1α, 2α) 2.4, (2α, 2β) 16.0, (2α, 3) = (2β, 3) = 5.6, (5α, 5β) 15, 4, (5α, 6) 2.7, (5β, 6) 10.2, (6, 10) 12.4, (7α, 7β) = (7α, 8) = 13.7, (7β, 8) 3.7, (8, 17) 5.1, (10, 1β) 3.4, (14, 15) 7.1 Hz.
[b] Overlapped signal.



Scheme 1

Table 2. ^{13}C N.m.r. spectral data.

	(1) (100 MHz, $CDCl_3$)	(2) (100 MHz, CD_3OD)	(3) (50 MHz, CD_3OD, $SiMe_4$)	(4) (50 MHz, CD_3OD, $SiMe_4$)
C-1	26.8	28.0	24.9	21.1
C-2	26.6	28.2	30.3*	29.9
C-3	126.1	128.8	126.3	124.6
C-4	137.5	141.9	133.5	133.9
C-5	31.8	29.1	38.3	34.0
C-6	49.1	51.3	61.9	92.3
C-7	46.4	47.9	44.2	40.2
C-8	38.5	40.4	39.7	36.1
C-9	40.1	41.7	52.2	50.2
C-10	51.7	53.7	48.1	52.0
C-11	35.3	37.0	34.1	28.9
C-12	28.2	29.0	30.8*	30.2
C-13	143.6	143.5	143.5	143.1
C-14	126.1	127.8	127.4	127.4
C-15	58.6	59.4	58.8	58.7
C-16	61.0	60.9	60.2	60.1
C-17	15.7	17.4	13.6	16.6
C-18	25.6	68.7	27.9	26.5
C-19	211.2	213.9	207.3	72.7
C-20	16.4	16.7	64.6	74.7

tion with ^{13}C n.m.r. data, indicates that in (**2**) the vinyl methyl of (**1**) is replaced by a hydroxymethylene group. Thus ^1H n.m.r. analysis [based on HNSD, 2D, and nuclear Overhauser effect (n.O.e.) experiments] fully corroborate structure (**2**) for pilosanone B. Moreover, (**1**) and (**2**) showed strong negative bands at 295 ($\Delta\varepsilon$ −0.86, EtOH) and 293 nm ($\Delta\varepsilon$ −0.79, EtOH) respectively in c.d. measurements, which signify the absolute configuration of both compounds to be of the *neo*-clerodane type.

The bicyclo[5.4.0]undecane diterpenoids (**1**) and (**2**), representing a possible link between the *ent*-labdadienyl cation (**5**) and portulal (**3**),[6] are demonstrated to occur as major constituents in *P. pilosa* L. This finding sharply contrasts with the case of *P. grandiflora* Hook, where portulal-type compounds represent the major constituents and the bicyclo[5.4.0]undecane diterpenoids are found only in minor amounts.[1] Clerodane-type diterpenoids are the major component in *P. cv. Jewel.*[5] As shown in the proposed biosynthetic scheme for the *Portulaca* plant (Scheme 1), the three species mentioned above produce the closely related diterpenoids in different ways depending on their metabolic abilities. Portulal (**3**) is the most advanced as far as the change of carbon skeleton is concerned, (**1**) and (**2**) being the metabolites of an intermediate stage. This fact provides evidence for the evolutional transition of the enzyme system in *Portulaca* plants and is interesting in connection with their chemosystematics.

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