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Novel Diterpenes with Bicyclo[5.4.0]undecane Skeleton from Portulaca grandiflora Hook, Possible Linking Intermediates in the Biosynthesis of Portulal

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Three new diterpenes with bicyclo[5.4.0]undecane skeleton were isolated from Portulaca grandiflora Hook and their structures have been elucidated by spectroscopic methods involving an extensive application of NMR techniques. The significance of these compounds in the consideration of biosynthesis of portulal is suggested.

In the continuation of our work on the diterpenoid constituents of Portulaca grandiflora Hook,[1,2] we have characterized three compounds with novel bicyclo-[5.4.0]undecane skeleton, which could situate midway in the biosynthesis of portulal 1, a plant-growth regulator,[3] and this communication deals with the elucidation of their structures.

The diterpenoid fractions obtained from the extract of the aerial part of P. grandiflora as described previously,[1,2] were separated by extensive chromatography giving three new constituents, which were designated as portulenone 2, portulenol 4 and portulene 5, with the other diterpenes.[2]

Portulenone 2 was isolated as a colorless oil: $[\alpha]_D^{11.5}$ -49.9 (c 1.22, EtOH), $C_{20}H_{30}O_5$ (m/z 350.2069; calcd 350.2046); UV(MeOH), ν_{max} 232 nm (ε 5,750); IR(film), ν_{max} 3400 and 1650 cm^{-1}. Acetylation of 2 afforded a triacetate, $C_{26}H_{36}O_8$ (m/z 476.2411; calcd 476.2410). Inspection of its ^1H and ^{13}C NMR spectra (cf. Fig. 1 and Table 1) indicated that two of the three hydroxyl groups present in 2 were comprised in the 5-hydroxy-3-hydroxymethyl-3-pentenyl side chain, a characteristic of Portulaca diterpenoids. The rest is secondary as evidenced by the appearance of a signal due to the proton attached to a hydroxyl-bearing carbon atom at δ 3.47 in the ^1H NMR spectrum. The observation of a vinylic methyl signal at δ 1.87 and a vinyl proton resonance at δ 6.31 in conjunction with the other spectral evidences (UV and IR) pointed the presence of an α-methyl-α,β-unsaturated ketonic group. The remaining oxygen atom must be etheric and this deduction is associated with the appearance of an AB quartet at δ 3.35 and 3.82 in the ^1H NMR, and of signals at δ 73.9 and 90.4 in the ^{13}C NMR spectra. In addition the ^1H NMR signal due to a secondary methyl group was observed at δ 0.88. These functional units were elaborated to the partial structures A - D by the application of 2D-COSY and HNSD techniques. Furthermore

the segments C and D were incorporated to the structure E implying also the stereochemical disposition of the substituents, since a long range coupling of W-letter type existed between one of the methylene protons of the ether ring and the methine proton next to the methyl group, and NOE was observed between the methyl protons and one of the methylene proton (δ 3.82). The connection of the segments A, B and E resulted in the formulation of two possible structures 2 and 3 for portulenone, of which the biogenetically unlikely structure 3 was rejected on the basis of the ^{1}H-selective decoupling experiment in the ^{13}C NMR spectrum. The irradiation of C-5 vinyl proton resonance decidedly deformed the C-6 signal at δ 90.4 but not the C-9 signal at δ 51.6. Thus the structure 2 is assigned for portulenone.

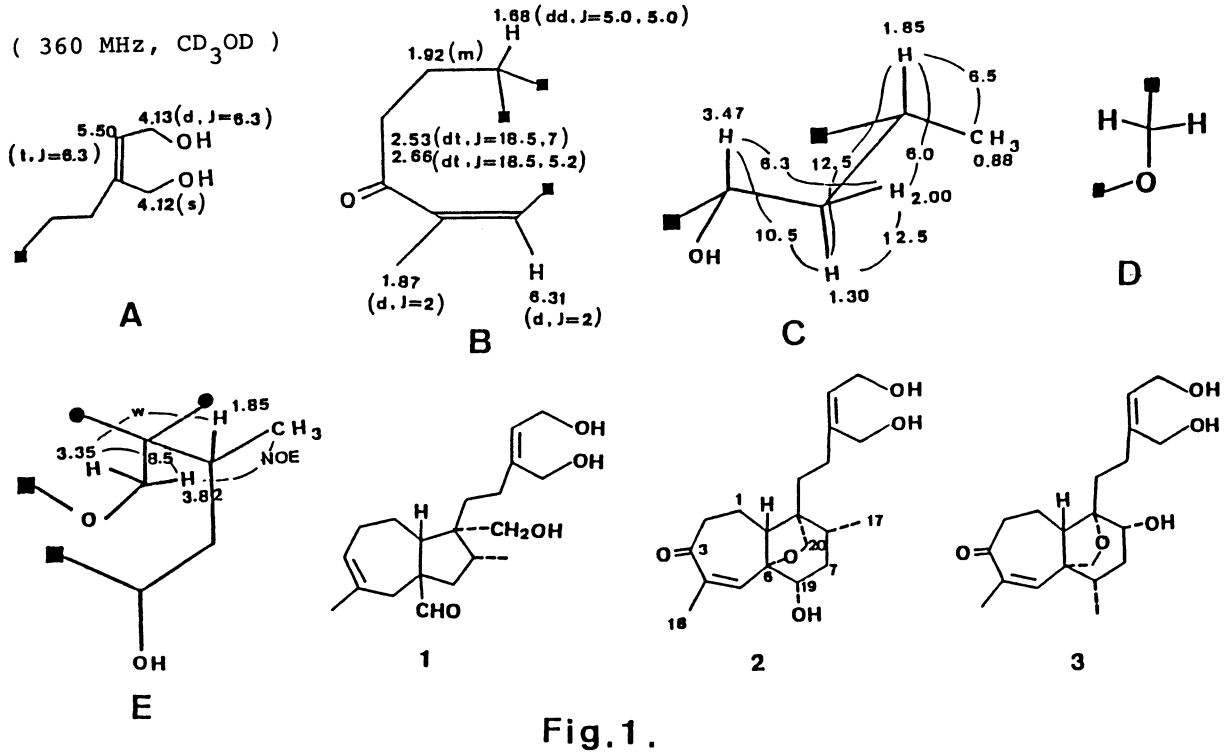


Fig.1.

Portulenol 4, obtained as an unstable colorless oil, $[\alpha]_D^{12.5}$ -57.4 (c 0.72, EtOH) has the molecular formula $C_{20}H_{32}O_5$ as revealed from MS measurements (EI, M^+ m/z 352.2257; calcd 352.2250. FAB, MH^+ m/z 353) and exhibited IR peaks (film) at 3400 and 1600 cm^{-1}. The comparison of ^{1}H and ^{13}C NMR spectra with those of 3 showed a good correspondance except the details related with A ring structure. The appearance of two signals due to vinylic protons at δ 5.58(dt) and 5.82(ddd) and a somewhat deshielded methyl proton resonance at δ 1.30 in the ^{1}H NMR suggested the presence of $\Delta^{2,3}$-double bond and 4-hydroxy group. This supposition was consonant with the observations of a long range coupling (J = 2.4 Hz) between H-3 and H-5 resonances and of the NOE enhancement between H-3 and the methyl protons. The assumption of the same carbon skeleton as in 2 led to the proposal of the formula for portulenol as 4 and this has been fully substantiated by the results of ^{1}H HNSD experiment depicted in 4a. However the stereochemistry at C-4

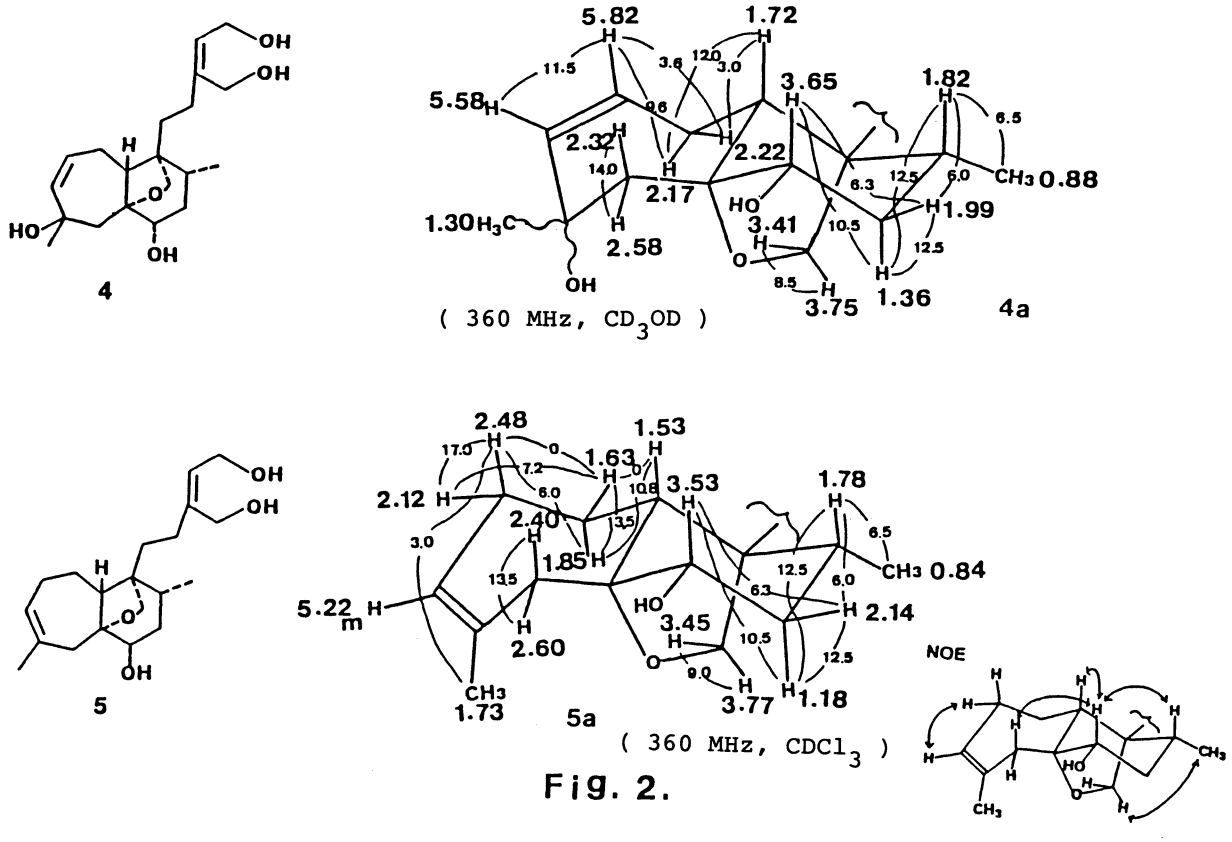


Fig. 2.

has remained unassigned.

The last compound, portulene 5, $[\alpha]_D^{12.5}$ -42.1 (c 0.83, EtOH), has the molecular formula, $C_{20}H_{32}O_4$ (EI-MS, M^+ m/z 336.2272; calcd 336.2300. FAB-MS, MH^+

Table 1. ^{13}C NMR data of compounds 1, 2, 4, and 5. (50 MHz, CD_3OD, TMS)

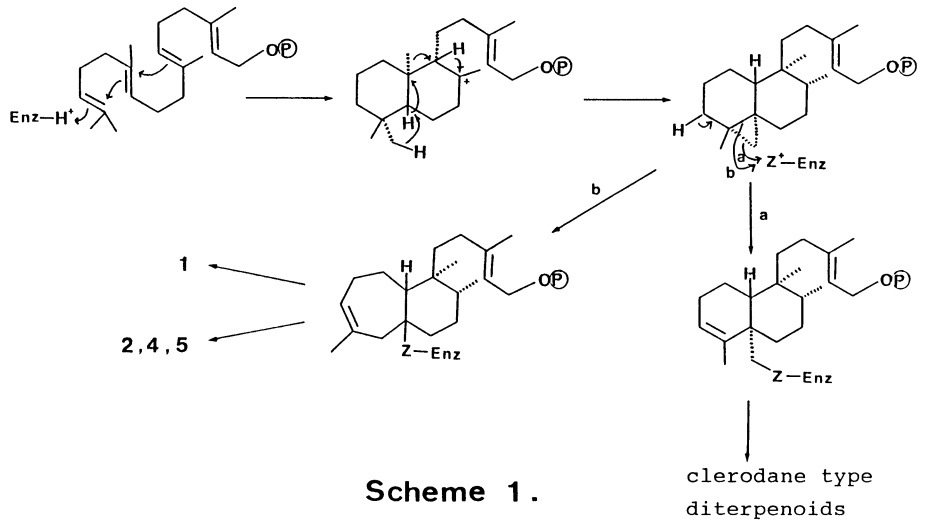
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
1	24.9	30.3*	126.3	133.5	38.3	61.9	44.2	39.7	52.2	48.1
2	20.7	43.3	209.3	136.7	136.7	90.4	39.4	35.5	51.6	50.3
4	24.3	129.9	137.0	83.9	39.8	88.5	37.9	35.3	51.3	52.7
5	21.1	29.9	124.6	133.9	34.0	92.3	40.2	36.1	50.2	52.0

	C-11	C-12	C-13	C-14	C-15	C-16	C-17	C-18	C-19	C-20
1	34.1	30.8*	143.5	127.4	58.8	60.2	13.6	27.9	207.3	64.6
2	29.4	30.1	142.7	127.3	58.6	59.9	16.5	20.7	76.2	73.9
4	28.4	29.8	142.8	127.2	58.5	60.0	16.6	24.6	73.8	73.5
5	28.9	30.2	143.1	127.4	58.7	60.1	16.6	26.5	72.7	74.7

Assingments of 1 and 5 were made with the aid of $^{13}C,^1H$-COSY.

m/z 337) which contains the oxygen atoms less than 4 by one. The ^{1}H and ^{13}C NMR spectra were very similar with those of 2 and 4 except the signals assigned to A ring portion. The presence of the trisubstituted double bond unit, reminiscent of that in 1, was inferred from the appearance of signals due to the vinyl methyl protons at δ 1.73 and due to the vinyl proton at δ 5.22(m) in the ^{1}H NMR spectrum. In fact the ^{13}C NMR resonances assigned to C-2, C-3, and C-18 showed a good correspondance to those of 1 in chemical shifts (Table 1) as well as the ^{1}H NMR features (cf. 5a). The structure 5 is reasonably assigned for portulene.

The occurrence of the bicyclo[5.4.0]undecane derivatives[4] in P. grandiflora thus disclosed[5] is interesting in connection with the biosynthesis of portulal 1. This fact suggests that the linking intermediate in the biosynthesis of 1 should be the compound with bicyclo[5.4.0]undecane skeleton rather than the bicyclo-[4.3.0]nonane, postulated previously.[3] Taking the demonstrated occurrence of clerodane diterpenes[1,6] into consideration we propose the scheme shown below as a possible biosynthesis route of the diterpenoids found in the Portulaca species.



Scheme 1.

References

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3) S. Yamazaki, S. Tamura, F. Marumo, and Y. Sato, Tetrahedron Lett., 1969, 359.

4) The occurrence of the diterpenoids with this carbon skeleton was reported: F. Bohlmann, and C. Zdero, Phytochemistry, 17, 487(1978); F. Bohlmann, M. Grenz, P. Wegner, and J. Jakupovic, Ann. Chem., 1983, 2008.

5) Although the direct evidence for the absolute configuration of these compounds is not available yet, it is probably of neo-clerodane type in view of the established absolute configuration of portulal 1[3] and portulide A.[1]

6) A. Ohsaki, N. Ohno, K. Shibata, T. Tokoroyama, and T. Kubota, Phytochemistry, in press (1986).

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