Communications to the Editor

[Chem. Pharm. Bull. 33(5)2171—2174(1985)]

DITERPENOID CONGENERS OF PORTULAL IN PORTULACA GRANDIFLORA HOOK

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In the survey of the minor diterpenoid constituents of Portulaca grandiflora Hook, four new compounds, portulic lactone (4), 3-hydroxyportulol ether (5), 5-hydroxyportulal (6), and 5-hydroxyportulic acid (7), were isolated and their structures, all of which have skeletons related to portulal (1), were elucidated on the basis of spectral evidence and chemical correlations.

KEYWORDS —— Portulaca grandiflora; Portulacaceae; portulic lactone; 3-hydroxyportulol ether; 5-hydroxyportulal; 5-hydroxyportulic acid; portulal ^{13}C-NMR

Portulal (1) is a diterpene isolated from Portulaca grandiflora as a plant-growth regulator.[1)] Having a unique perhydroazulenoid structure,[2)] it is intriguing from the viewpoint of biosynthesis and a speculative scheme has been proposed. From this interest in the biosynthesis[3)] as well as the biological activities, we examined the minor constituents of Portulaca grandiflora and isolated four new congeners of 1. In this communication we elucidate their structure.

All plants of Portulaca grandiflora were extracted with methanol and the extract was percolated successively with petroleum ether and ether. The separation of the ether extract by Sephadex LH-20 permeation and repeated RP-8 chromatography afforded the four new diterpenes, portulic lactone (4), 3-hydroxyportulol ether (5), 5-hydroxyportulal (6), and 5-hydroxyportulic acid (7) in addition to portulal (1), portulol (2),[4)] and portulic acid (3).[5)]

Portulic lactone (4), colorless oil, $[\alpha]_D^{26.5}$ = + 23.8° (c 0.58, EtOH) showed the $M^+ - H_2O$ peak at m/z 334.2142 (Calcd, 334.2142 for $C_{20}H_{30}O_4$) in the MS and exhibited IR bands at 3400 and 1745 cm^{-1}. The comparison of the ^1H-NMR spectrum (Table I) of 4 with that of 1 reveals that the former has most of the features in common with the latter but they are discriminated in that the vinyl methyl and vinyl protons signals of the latter are replaced by a methyl singlet at δ 1.46 in the former. This spectral evidence as well as the ^{13}C-NMR data suggested that 4 could be the (19→4)-lactone derived from portulic acid (3). In fact 4 was identical with the product obtained from 3[6)] by acid-treatment (camphorsulfonic acid/benzene under refluxing) or iodolactonization followed by reduction with Bu_3SnH.

3-Hydroxyportulol ether (5), colorless oil, $[\alpha]_D^{20}$ +11.2°(c 0.448, EtOH); MS (M^+-H_2O), m/z 336.2264 (Calcd, 336.2299 for $C_{20}H_{32}O_4$); IR(neat), 3350, 1650, and

1020 cm^{-1}, exhibited structure characteristics similar to 4 in the ^{1}H- and ^{13}C-NMR spectra (Tables I and II). The distinction was the presence of a methylene and a methine group, both having oxygen functions, which were assigned to C-19 as the part of a cyclic ether ring and to C-3 attached with a hydroxyl group. Although the signal of the C-3 proton was masked by that of the C-20 methylene protons, the corresponding resonance in the tetraacetate of 5 was observable at δ 4.75 as a broad singlet. The placement and the stereochemistry of the hydroxyl group at C-3 was based on the ^{13}C-NMR evidence$^{8)}$ and synthetic experiment (vide infra). The structure thus deduced has been confirmed by the derivation of 5 from 2.$^{4)}$ When 2 was treated with m-chloroperbenzoic acid in CH_2Cl_2-THF at -78°C, oxidation occurred regioselectively and, after the usual workup, 5 was obtained directly. The epoxidation plausibly$^{9)}$ takes place from the α-side of the molecule followed by the ring cleavage through the back-side attack at C-4 of the 19-hydroxyl group.

5-Hydroxyportulal (6), colorless oil, $[\alpha]_D^{12.5}$ -79.1°(c 0.685, EtOH); MS(M^+-H_2O), m/z 334.2142 (Calcd, 334.2142 for $C_{20}H_{30}O_4$), IR(neat), 3300, 1720, and 1020 cm^{-1}, exhibited a series of the fragmentation peaks differing from that of 1 by 16 mass units in the mass spectrum. Accordingly 6 was presumed to be a portulal analog which has an additional hydroxyl group. In the ^{1}H NMR-spectrum of 6, the signal due to the proton attached to the hydroxyl-bearing carbon atom overlapped with that of the C-15 proton, but the tetraacetate of 6 showed a corresponding signal at δ 5.34 as a sharp singlet. Furthermore in the 360 MHz NMR spectrum of 6, the methine proton signal was separately observable at δ 4.24. The other features in the ^{1}H-NMR spectrum of 6 with reference to 1 were that the resonance of the C-3 vinyl proton was deshielded by 0.26 ppm and the C-20 hydroxymethylene protons became nonequivalent, one of the protons being deshielded by 0.16 ppm, the other being unaffected. This evidence$^{10)}$ in conjunction with ^{13}C-NMR data, indicate that the secondary hydroxyl group in 6 should be located at C-5. The α-configuration of the hydroxyl group clearly explains the nonequivalence of the C-20 methylene proton signal (vide ante).$^{11)}$ That 6 has the same carbon skeleton as 1 was confirmed ultimately by chemical correlation. When the acetate (9) derived from 6 by 1. oxidation with 2,3-dichloro-5,6-dicyano-benzoquinone and 2. acetylation, was treated with Li /liq.NH_3, the hydrogenolysis product 8 was obtained through concomitant reduction of the formyl group and the hydrolysis of the 20-acetoxyl group. Compound 9 was found to be identical with the product obtained from 1 by 1. DDQ oxidation and 2. lithium aluminum hydride reduction.

5-Hydroxyportulic acid (7), colorless oil, $[\alpha]_D^{12.5}$ -87.6°(c 0.276,EtOH); MS (M^+ -$2H_2O$), m/z 332.2016 (Calcd, 332.1988 for $C_{20}H_{28}O_4$); IR(neat), 3260 and 1700 cm^{-1} was deduced to be the carboxylic acid corresponding to 6 since the ^{1}H- and ^{13}C-NMR spectra were almost superimposable on those of 6 except that the formyl group signal of the latter was replaced by the carboxyl group signal. This deduction was verified by the derivation of 7 by sodium chlorite oxidation of 6.

All of the four new constituents of Portulaca grandiflora Hook dealt with in this paper have carbon skeletons common to portulal 1. The new sites of oxygenation at C-3 and C-5 are noted in the compounds 5 and, 6 and 7 respectively. All of the compounds carry the caracteristic 2-(1,4-dihydroxy-2-butenyl) system in side chains which suggests the presence of a specific enzyme responsible for the oxygenation process.

Table I. ^{1}H-NMR Spectra (100 MHz, CD_3OD)

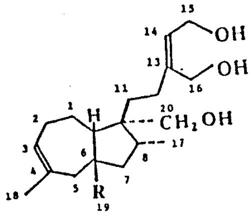
Compounds	3-H	5-H	14-H	15-H	16-H	17-H	18-H	19-H	20-H
1	5.24 (m)		5.50 (t,J=6)	4.17 (d,J=6)	4.11 (s)	0.96 (d,J=6)	1.70 (s)	9.44 (s)	3.54 (s)
4			5.65 (t,J=6)	4.20 (d,J=6)	4.20 (s)	1.02 (d,J=6)	1.46 (s)	---	3.60 (s)
5	3.50 (?)		5.45 (t,J=6)	4.12 (d,J=6)	4.10 (s)	0.98 (d,J=6)	1.26 (s)	3.70 (s)	3.50 (s)
6	5.50 (m)	4.23? (s)	5.50 (t,J=6)	4.20 (d,J=6)	4.16 (s)	1.00 (d,J=6)	1.80 (s)	9.49 (s)	3.55, 3.70 (ABq,J=12)
7	5.56 (m)	4.44 (s)	5.60 (t,J=6)	4.22 (d,J=6)	4.18 (s)	1.08 (d,J=6)	1.84 (s)	---	3.50, 3.80 (ABq,J=12)

Table II. ^{13}C-NMR Spectra (25MHz, CD_3OD)

Compounds	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
1	25.8	31.1*	127.7	134.3	39.0	62.8	45.0	40.5	53.1	48.9
4	25.8	25.8	46.4	86.7	45.9	53.7	42.6	41.9	52.6	58.5
5	20.5	34.1*	75.9	87.5	43.2	51.8	44.6	42.2	53.4	60.5
6	26.2	32.3	132.1	137.2	76.8	66.0	39.9	41.8	53.0	48.8
7	26.2	32.2	130.6	138.5	77.4	61.9	40.3	46.5	52.6	49.3

Compounds	C-11	C-12	C-13	C-14	C-15	C-16	C-17	C-18	C-19	C-20
1	34.8	31.6*	144.3	128.2	59.6	61.0	14.4	28.8	208.0	65.5
4	33.4	30.5	144.1	128.2	59.6	60.9	14.8	29.8	189.4	65.1
5	34.8*	30.9	144.4	128.2	58.7	61.1	15.2	28.2	86.4	65.2
6	35.5	31.1	144.1	128.3	59.6	61.0	14.1	27.4	204.4	66.7
7	35.6	31.2	144.3	128.3	59.6	61.0	14.0	27.7	181.7	66.9

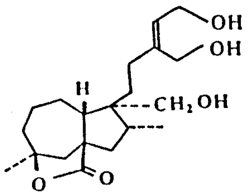
*: The assignments are interconvertible.



1 : R = CHO

2 : R = CH_2OH

3 : R = CO_2H



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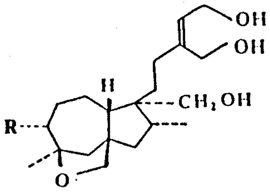
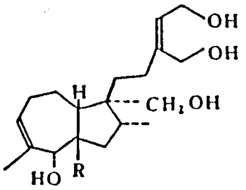
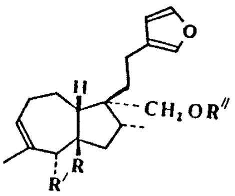


5 : R = OH



6 : R = CHO

7 : R = CO_2H



8 : R = CH_2OH, R'= R"= H

9 : R = CHO, R'= OAc, R"= Ac

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6) Prepared by the oxidation of 1 with $NaClO_2$.[7)]

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8) The assignments of the ^{13}C-NMR spectra for portulal and the related compounds were carried out by comparing the data to a number of the derivatives and by using appropriate measurement techniques (off-resonance, INEPT and selective decoupling, 2D ^{13}C-^{1}H correlation, etc.) in collaboration with Mr. Naoki of the Suntory Institute for Bioorganic Reserch. Its compilation will be published elsewhere.

9) E. Toromanoff, Tetrahedron, 36, 2809 (1980).

10) The ^{1}H-NMR of 6 was investigated in 360 MHz by spin decoupling and 2D techniques and all of the signals were assigned. The result is consistent with the formulation of 6 as 5-hydroxyportulal. We thank Mr. H. Naoki and Dr. Y. Naya for this experiment.

11) Inspection of the molecular model reveals that the cycloheptene ring of 6 exists in a twist form due to fusion with the cyclopentane ring, and in this conformation the C-5α-hydroxyl group is situated near enough to the C-20 hydroxymethylene group to have anisotropic influence. Moreover the 5β-proton almost lies in the plane of the double bond and this explains why the allyl coupling of the C-5 proton was not observed.

(Received March 22, 1985)