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PORTULIDE, A CLERODANE DITERPENOID FROM PORTULACA GRANDIFLORA HOOK

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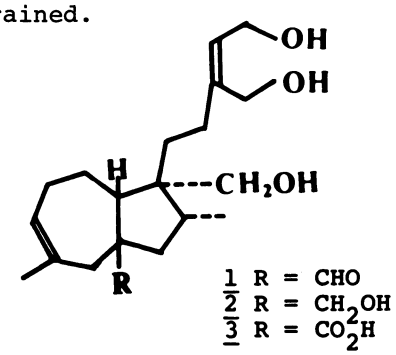
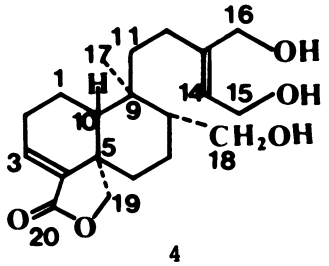
A clerodane diterpene, portulide has been isolated firstly from Portulaca grandiflora Hook and the structure also been elucidated on the basis of spectral evidences and chemical correlation.

The diterpene plant-growth regulator portulal 1, found in Portulaca grandiflora Hook, has a unique structure, perhydroazulenoid skeleton with clerodane-type substitution, and a speculative biosynthetic scheme has been proposed for it.[1] The unintelligible transformation involved intrigued us to investigate the minor constituents of the plant for the purpose of gaining the insight into the problem and we have confirmed firstly the occurrence of a clerodane diterpene, designated as portulide, in addition to portulal 1, portulol 2,[2] portulic acid 3,[3] and a number of new diterpene with the portulal skeleton.[4]

The neutral extract (2.026 g) obtained from the aerial part of Portulaca grandiflora Hook by reported procedure[5] was separated by chromatography on silica gel columns. The fraction eluted with EtOAc-EtOH (4:1) was rechromatographed giving portulide 4 (30 mg) as colorless amorphous solid: $[\alpha]_D^{29.5}$ -151.1°(c 0.068, EtOH); MS(20 eV), m/z($M^+ - H_2O$) 332.1998, Calcd for $C_{20}H_{28}O_4$, 332.1988. In the IR spectrum (neat), 4 exhibited the absorption bands due to hydroxyl groups at 3300 and due to γ-lactone ring at 1760 cm^{-1}. The inspection of ^1H and ^{13}C NMR (Tables 1 and 2) suggested the presence of the same 2-(1,4-dihydroxy-2-butenyl)ethyl side chain as in 1 and the replacement of the secondary methyl group at C-8 by a hydroxymethylene group. The appearance of the olefinic proton at rather lower field (δ 6.75) indicated the ring double bond conjugated with the γ-lactone, possibly strained.



1 R = CHO
2 R = CH_2OH
3 R = CO_2H



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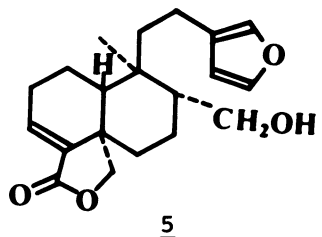

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while this grouping was hard to reconcile with the portulal type skeleton. In conjunction with the presence of a tertiary methyl resonance at a shielded position (δ 0.66), the fact implicated that the ring system of 4 might be different from that of 1. Thus the result of the detailed decoupling experiment in 400 MHz ^{1}H NMR spectroscopy has accommodated with the assignment of clerodane formula 4 for portulide. Specially, the presence of W-letter type coupling between C-6 and C-19 protons indicates that 4 must have the trans ring junction. The structure 4 deduced for portulide has been confirmed by a chemical correlation. Treatment of 4 with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone[6] in t-butanol at 40-50 °C gave a furan derivative 5. The product was found to be identical with the compound which had been derived[7] by the lactonization of trans clerodane diterpene 6 (5: C-19, -CH_2OH; C-20, -CO_2H) obtained from Dodonaea attenuata A. Cunn. (Sapindaceae). Moreover both samples of 5, prepared from 4 and 6, showed strong negative bands at 242 nm in the CD measurements[8] which signify the absolute configuration of 4 and 6[7] to be that of neo-clerodane type.[9] Thus it turns out that portulide 4 has the absolute configuration corresponding to portulal,[1] and the same biogenetic origin of both constituents would be suggested. This fact provides a circumstancial evidence in the consideration of biosynthesis of portulal 1.

Table 1. ^{1}H NMR spectrum of portulide 4 (400 MHz, CD_3OD)

Proton		Proton		Proton		Proton	
1β	1.77, ddd	6β	1.22, dddd	10	1.82, d	16	4.13, s
1α	1.13, dddd	6α	1.92, ddd	11	1.54, ddd	17	0.66, s
2β	2.25, dddd	7β	2.02, dddd	12	2.22, m	18	3.80, dd
2α	2.40, dddd	7α	1.68, dddd	14	5.51, t		3.26, dd
3	6.75, dd	8	1.78, m	15	4.13, d	19β	4.45, d
						19α	4.03, dd

Proton coupling constants in Hz: 1α,1β = 12.0; 1α,2α = 3.8; 1α,2β = 12.0; 1α,10 = 12.0; 1β,2α = 2.9; 1β,2β = 3.8; 2α,2β = 15.9; 2α,3 = 7.3; 2β,3 = 2.0; 6α,6β = 13.2; 6α,7α = 3.4; 6β,7α = 3.4; 6β,7α = 13.2; 6β,7β = 3.8; 6β,19α = 1.8; 7α,7β = 13.2; 7α,8 = 13.2; 7β,8 = 3.8; 14,15 = 6.8; 19α,19β = 8.2

Table 2. ^{13}C NMR spectrum of portulide 4 (25.0 MHz, CD_3OD)[10]

Carbon		Carbon		Carbon		Carbon		Carbon	
1	20.7	5	47.7	9	40.2	13	144.0	17	19.9
2	29.1	6	36.1	10	46.3	14	128.3	18	64.6
3	138.5	7	24.5	11	38.4	15	60.9	19	74.2
4	140.6	8	50.3	12	29.7	16	59.5	20	172.6

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References

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10) The signals are assigned on the basis of off-resonance multiplicities and by the comparison of shift values with data in the literature.

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