IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1750 (γ-lactone), 1710 (C=O). ^{13}C NMR: see Table 1. ^{1}H NMR: see Table 2.

EIMS (70 eV, direct inlet) *m/z* (rel. int.): 248 (52), 233 (7), 230 (8), 219 (10), 215 (12), 187 (13), 175 (18), 174 (17), 147 (10), 137 (100), 125 (22), 124 (22), 112 (43), 110 (22), 109 (48), 107 (13), 105 (13). HRMS *m/z*: 248.1385 ($C_{15}H_{20}O_3$; $[M]^+$), 230.1266 ($C_{15}H_{18}O_2$; $[M-H_2O]^+$), 215.1073 ($C_{14}H_{15}O_2$; $[230-Me]^+$), 137.0975 ($C_9H_{13}O$, 100%).

Transformation of istanbulin A to istanbulin B. To a soln of istanbulin A (68.7 mg) in $CHCl_3$ (15 ml) was added 57% HI (0.2 ml) and the soln was refluxed (1.5 hr). This reaction mixture was cooled, poured into 0.01 M $Na_2S_2O_3$ (50 ml), extracted with $CHCl_3$ (3 × 25 ml), dried and concd *in vacuo* yielding istanbulin B (45 mg) which was identified with authentic sample by mmp, TLC, IR, NMR spectral data.

4-hydroxy-3-methoxyacetophenone (acetovanillone). Identified by TLC, IR, ^{1}H NMR by comparison with an authentic sample.

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CLERODANE DITERPENOIDS FROM *PORTULACA* CV JEWEL

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Key Word Index—*Portulaca* cultivar; Portulacaceae; diterpene; *trans*-clerodane; portulides A–D.

Abstract—Three *trans*-clerodane diterpenes were isolated from the aerial part of the *Portulaca* cv Jewel. Their structures were elucidated by spectroscopic methods and chemical correlations.

INTRODUCTION

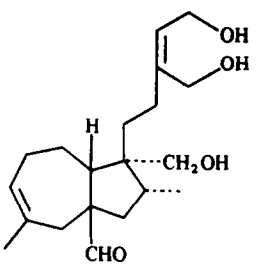
Among the known constituents of *Portulaca* plants are portulal **1**, a plant growth regulator [1–3] and the minor diterpenoid congeners of *Portulaca grandiflora* Hook. [4, 5]. In this paper we report on the constituents of the *Portulaca* cv Jewel, the flower of which is similar to that of *Portulaca grandiflora* Hook. except that it is single-petalled. The two plants also differ in chromosome number [6].

RESULTS AND DISCUSSION

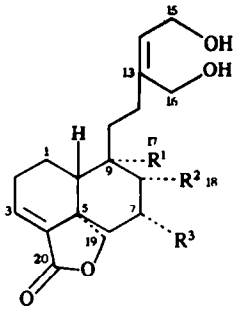
An ethyl acetate extract of *Portulaca* cv Jewel was separated by extensive chromatography. Portulide A **2**, previously reported as 'portulide' [4], was isolated as a major constituent. In addition, three new apparently closely related constituents, portulide B **3**, portulide C **4** and portulide D **5**, of which **3** represented the other major compound, were obtained and characterized on the basis of spectroscopic analyses and chemical correlations.

The new compounds **3–5** have the molecular formulae $C_{20}H_{28}O_3$, $C_{20}H_{28}O_4$ and $C_{20}H_{26}O_4$, respectively, deduced from the $[M-H_2O]^+$ peaks in high resolution mass spectra. The molecular ion peaks were ascertained by FAB mass spectroscopy in glycerol. The IR spectra indicated the presence of hydroxyl groups and $\Delta^{2,3}$-butenolide rings in every compound.

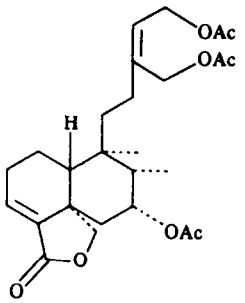
In the ^{1}H NMR spectrum portulide B **3** exhibited



1



2 R^1 = Me, R^2 = CH_2OH, R^3 = H
3 R^1 = Me, R^2 = Me, R^3 = H
4 R^1 = Me, R^2 = Me, R^3 = OH
5 R^1 = Me, R^2 = CHO, R^3 = H



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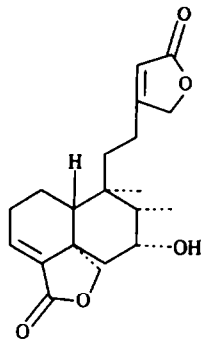

7

AB-type signals at δ3.87 and 4.25, the former being further split with a coupling constant of 2 Hz, due to the methylene protons of the lactone ring, as in compound **2**. On the other hand, the signal of the secondary methyl protons at δ0.82 (H-18) was observed instead of resonances due to the hydroxy methylene protons at δ3.26 and 3.80 ppm in **2**. The other signals were very similar to those of **2**. Correspondingly, in the ^{13}C NMR spectrum of **3**, (Table 1), a methyl carbon signal at δ15.6 (C-18) was observed instead of the methylene carbon signal at δ63.8 in **2**. Moreover the methine carbon signal (C-8) was shielded by 13 ppm from that of **2**. Thus the spectral data were consistent with the assignment of the structure as **3**.

The second compound, portulide C **4**, has an additional oxygen function to **3**. It appears to be a secondary hydroxyl group, since **4** gave the triacetate **6** on acetylation. The ^{1}H NMR signal due to the proton attached to the acetoxyl-bearing carbon atom of **6** was observed at δ5.28 as a multiplet. In the ^{1}H NMR spectrum of **4**, H_α-19 of the butenolide ring showed an w-type coupling with H_β-6 in the same way as in **2** and **3**, while the H_β-19 signal was shifted downfield to δ5.32. In addition, the signal of an axial methyl group at C-9 was deshielded by 0.3 ppm as compared with that of **3**. The results of the double resonance experiment with **4** revealed that an axial hydroxy group existed at the C-7 position and this explained the deshielding of the C-9 methyl resonance. The ^{1}H NMR data of portulide C **4** showed a good correspondence with those of **7**, isolated from *Baccharis trimera* (Less.) DC [7]. Thus structure **4** is assigned to portulide C and the ^{13}C NMR data (Table 1) are also consistent with this.

The ^{1}H NMR spectrum of portulide D **5** resembled closely that of **2** except that the proton signals of the C-18 methylene group were replaced by a formyl proton signal at δ9.72. In the ^{13}C NMR of **5**, the signal of the methine carbon (C-8) appeared at δ53.8, being deshielded by 17.2 ppm as compared with that of **3**. Therefore **5** is the C-18 formyl derivative of **2** and this was confirmed by the conversion of **5** to **2** through $NaBH_4$ reduction.

All four constituents of *Portulaca* cv Jewel have a

Table 1. ^{13}C NMR spectra of clerodane diterpenoids (50 MHz)

Carbon	2 CD_3OD	3 $CDCl_3$	4 CD_3OD	5 $CDCl_3$
C-1	20.0	19.6	19.8	18.6
C-2	28.5	28.5	28.9	28.4
C-3	137.6	136.0	136.9	136.2
C-4	139.8	138.6	140.5	137.9
C-5	46.9	45.7	46.4	45.2
C-6	35.3	36.3	41.7	37.4
C-7	23.7	27.8	73.1	19.2
C-8	49.7	36.6	41.8	53.8
C-9	39.4	38.8	39.7	39.0
C-10	45.4	48.9	48.5*	47.9
C-11	37.6	34.5	38.5	31.7
C-12	28.9	27.7	28.6	27.4
C-13	143.1	143.5	143.2	142.6
C-14	127.5	126.2	127.4	126.7
C-15	58.7	58.2	58.6	58.2
C-16	60.1	60.4	60.2	60.0
C-17	19.1	17.8	20.1	19.0
C-18	63.8	15.6	12.4	205.0
C-19	73.4	72.0	74.3	71.3
C-20	171.9	169.8	172.5	168.9

Assignments of ^{13}C NMR chemical shifts were made with the aid of off-resonance and INEPT experiments.
*Pyridine-d_5.

2-(1, 4-dihydroxy-2-butenyl) sidechain which is characteristic of the constituents of *Portulaca grandiflora* Hook. However, they are all clerodanes whereas most of the constituents of *Portulaca grandiflora* are perhydroazulenoids.

EXPERIMENTAL

^{1}H NMR spectra were measured at 200 MHz for ^{1}H NMR and at 50 MHz for ^{13}C NMR with TMS as internal standard: EI mass spectra on a ionization voltage at 70 eV: TLC was performed on silica gel plates (Merck, Kiesel gel 60, F_{254}), etc.

Plant material. The seeds of *Portulaca* cv Jewel were purchased from Sakata seed company (Tokyo, Japan), and plants were grown at the Plant Garden, Faculty of Science, Osaka City University, and collected at the end of August 1983.

Extraction and isolation of diterpenoids. The aerial parts of fresh plants (27 kg) were ground with MeOH and kept at room temp. for several weeks. After filtration, the filtrate was evaporated to one-tenth of the original volume, treated with hexane and extracted with EtOAc. The residue (120 g) was chromatographed on silica gel. Elution with $CHCl_3$–MeOH (19:1) gave fractions containing diterpenoids and these were separated by repeated chromatography (Merck silica gel of 230–400 mesh, RP-8, and prep. TLC) affording the four diterpenes, portulide A **2** (17 g), portulide B **3** (20 g), portulide C **4** (0.5 g), portulide D **5** (0.2 g). Portulide A **2** was identified by comparison of ^{1}H NMR, ^{13}C NMR, IR and mass spectra with those of 'portulide' [4].

Portulide B **3**: colourless oil; $[\alpha]_D^{22.5}$ − 110.9 (MeOH; *c* 1.89); $[\theta]_{247}$ − 24420 (EtOH); IR ν^{CHCl_3} cm^{-1}: 3245, 1760, 1660; ^{1}H NMR ($CDCl_3$): δ0.56 (3H, *s*, H-17), 0.82 (3H, *d*, *J* = 7 Hz, H-18), 3.87 (1H, *dd*, *J* = 8, 2 Hz, H_α-19), 4.08 (2H, *s*, H-16), 4.11 (2H, *d*, *J* = 7 Hz, H-15), 4.25 (1H, *d*, *J* = 8 Hz, H_β-19), 5.52 (1H, *t*, *J* = 7 Hz, H-14), 6.67 (1H, *dd*, *J* = 7, 2 Hz, H-3); HRMS *m/z* 316.2008 $[M - H_2O]^+$, calc. for $C_{20}H_{28}O_3$; FAB-MS (glycerol) *m/z* 335 $[MH]^+$.

Portulide C **4**: mp 191–192°; $[\alpha]_D^{22.5}$ − 113.0, (MeOH; *c* 1.24); $[\theta]_{227}$ − 23660 (EtOH); IR ν^{CHCl_3} cm^{-1}: 3375, 1760, 1660; ^{1}H NMR (CD_3OD): δ0.85 (3H, *s*, H-17), 1.03 (3H, *d*, *J* = 7 Hz, H-18), 1.36 (1H, *ddd*, *J* = 14, 3, 2 Hz, H_β-6), 2.19 (1H, *dd*, *J* = 14, 3 Hz, H_α-6), 3.91 (1H, *dd*, *J* = 8, 2 Hz, H_α-19), 3.98 (1H, *m*, H-7), 4.07 (2H, *s*, H-16), 4.10 (2H, *d*, *J* = 7 Hz, H-15), 5.32 (1H, *d*, *J* = 8 Hz, H_β-19), 5.43 (1H, *t*, *J* = 7, H-14), 6.63 (1H, *dd*, *J* = 7, 2 Hz, H-3); HRMS *m/z* 332.2016 $[M - H_2O]^+$, calc. for $C_{20}H_{28}O_4$; FAB-MS (glycerol) *m/z* 351 $[MH]^+$. Portulide C triacetate **7**: ^{1}H NMR ($CDCl_3$) 0.84 (3H, *s*, H-17), 0.90 (3H, *d*, *J* = 7 Hz, H-18), 2.04 (6H, *s*, 15,16-OAc), 2.08 (3H, *s*, 7-OAc), 3.91 (1H, *dd*, *J* = 8, 2 Hz, H_α-19), 4.63 (2H, *s*, H-16), 4.64 (2H, *d*, *J* = 7 Hz, H-15), 4.80 (1H, *d*, *J* = 8 Hz, H_β-19), 5.28 (1H, *m*, H-7), 5.52 (1H, *t*, *J* = 7 Hz, H-14), 6.71 (1H, *dd*, *J* = 7, 2 Hz, H-3).

Portulide D **5**: colourless oil; $[\alpha]_D^{22.5}$ − 147.9 (MeOH; *c* 0.83); $[\theta]_{246}$ − 13630 (EtOH); IR ν^{CHCl_3} cm^{-1}: 3380, 1760, 1740, 1660; ^{1}H NMR ($CDCl_3$): δ0.84 (3H, *s*, H-17), 3.96 (1H, *dd*, *J* = 8, 2 Hz, H_α-19), 4.16 (2H, *d*, *J* = 7 Hz, H-15), 4.20 (2H, *s*, H-16), 4.36 (1H, *d*, *J* = 8 Hz, H_β-19), 5.62 (1H, *t*, *J* = 7 Hz, H-14), 6.78 (1H, *dd*, *J* = 7, 2 Hz, H-3), 9.72 (1H, *d*, *J* = 3 Hz, H-18); HRMS *m/z* 330.1806 $[M - H_2O]^+$ calc. for $C_{20}H_{26}O_4$; FAB-MS (glycerol) 349 $[MH]^+$. Reduction of **5** ($NaBH_4$–MeOH, at room temp. for 1 hr) gave **2** (80%).

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