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STRUCTURE OF PORTULAL

Sunao Yamazaki and Saburo Tamura
Department of Agricultural Chemistry
Faculty of Agriculture, The University of Tokyo
Bunkyo-ku, Tokyo, Japan
Fumiyuki Marumo and Yoshihiko Saito
The Institute for Solid State Physics, The University of Tokyo
Roppongi, Minato-ku, Tokyo, Japan

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Portulal[1], a neutral component isolated from Portulaca grandiflora Hook., has unique plant growth regulating activities. It inhibits elongation of Avena coleoptile sections induced by indoleacetic acid, whereas it accelerates adventitious root formation of Azukia epicotyl cuttings[2)3)].

Portulal, $C_{20}H_{32}O_4$, m.w. 336, m.p. 113°, $[\alpha]_D^{23}$ -50°(ethanol, c=5.0), has the following spectral properties: UV, λ_{max}^{EtOH} 285 mμ (ε 27); IR, ν_{max}^{Nujol} 3260, 2720, 1720, 1030 cm^{-1}; NMR[4)], δ 0.98(3H, d), 1.70(3H, s), 3.60(2H, s), 4.15(2H, d and 2H, s, overlapping), 5.30(1H, m), 5.55(1H, t), 9.60(1H, s) and 1.1-2.8(approximately 14 protons, unascertainable because of complex overlapping or incomplete resolution of multiplets). These suggest the presence of a secondary methyl, a vinyl methyl, three primary hydroxyls, two ethylenic double bonds, and an isolated tertiary aldehyde.

The molecular structure, stereochemistry and absolute configuration of this compound have been established by a three-dimensional X-ray diffraction study on its p-bromophenylsulfonylhydrazone, $C_{26}H_{37}O_5N_2SBr$, m.p. 170°.

The crystals are orthorhombic, space group $P2_12_12_1$, with four molecules in a cell of dimensions: a=10.68, b=36.98 and c=6.67 Å. Intensities of the three-dimensional reflections were measured visually from equi-inclination

Weissenberg photographs around the a and c axes taken with Ni-filtered Cu Kα radiation. In total, 2089 reflections were collected and converted into |F| values in the usual way. No absorption correction was made.

The structure was solved by the heavy atom method. The three-dimensional sharpened Patterson map gave clear evidence for the location of the bromine and sulfur atoms. These were used to derive phases for the first electron density map, and the positions of 26 out of 33 light atoms in the empirical formula were found. The successive Fourier syntheses revealed all the atomic positions. Parameters were refined by the least-squares method. The reliability factor is 13.5 per cent at the present stage[5]. The absolute configuration was determined by use of the anomalous dispersion effect of the bromine atom for Cu Kα radiation ($\Delta f' = -0.9$, $\Delta f'' = 1.5$). Some of the calculated intensities and the observed relations between $(hk\ell)$ and $(h\bar{k}\ell)$ are compared in Table 1.

TABLE 1

Determination of the Absolute Configuration

Indices	$\lvert Fc(hk\ell)\rvert^2$	obs.	$\lvert Fc(h\bar{k}\ell)\rvert^2$
1 2 1	5682	>	5079
1 3 1	2569	<	2895
1 4 1	3560	>	3120
2 4 1	3486	<	4030
4 10 1	343	<	606
5 9 1	399	>	283

The structure of portulal p-bromophenylsulfonylhydrazone molecule viewed along the c axis is illustrated in Fig. 1. Therefore, portulal has the stereochemical structure given in Fig. 2 (i) and (ii). The four asymmetric carbon atoms have 6(S), 8(R), 9(R) and 10(R) configurations, respectively (Prelog's notation)[6].

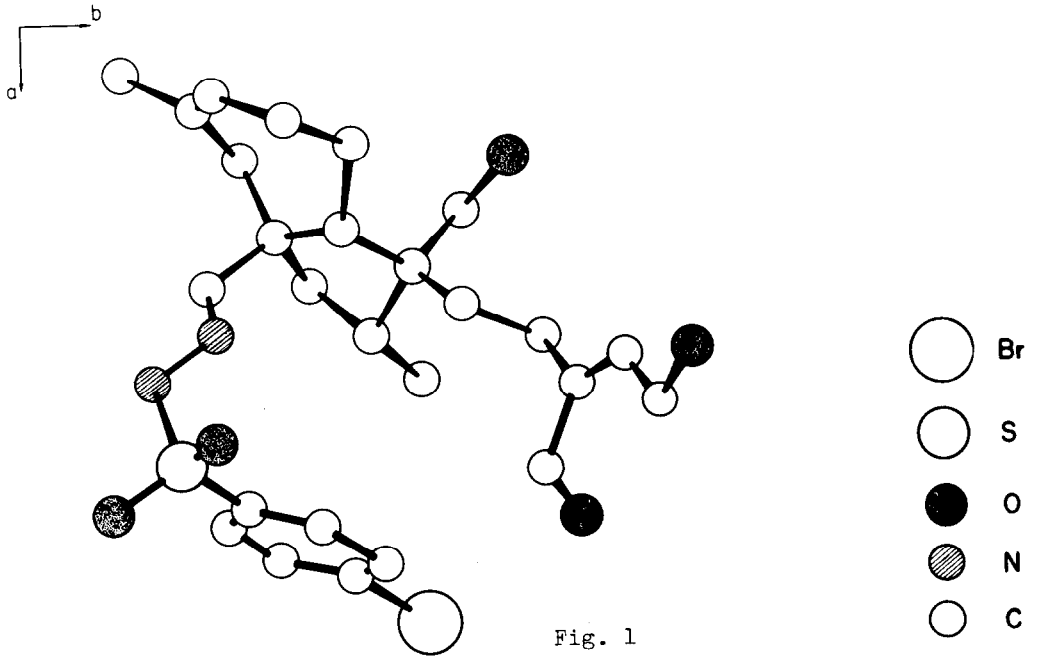
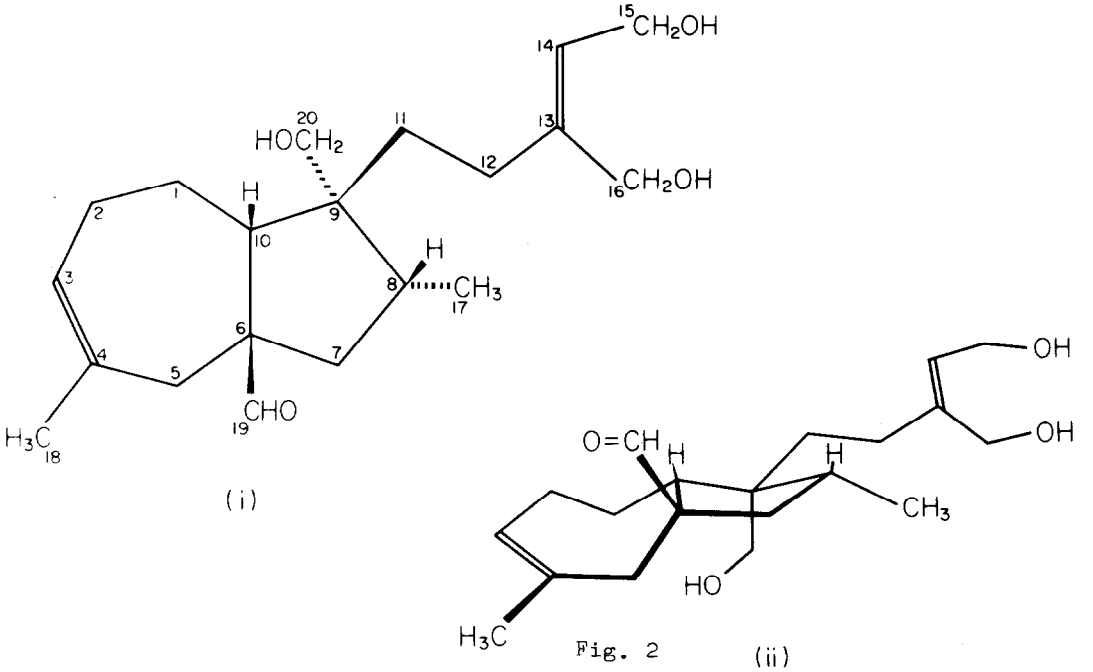


Fig. 1



(i)

Fig. 2

(ii)

Portulal belongs to a new type of bicyclic diterpene containing a perhydroazulene nucleus[7]. The carbon skeleton seems to originate from four isoprene units, but it conflicts with the Ruzicka's rule, suggesting occurrence of rearrangement from geranyl-geranyl (or geranyl-linalyl) pyrophosphate, the common diterpenoid precursor. Fig. 3 shows a plausible scheme of the biogenetical route of this compound.

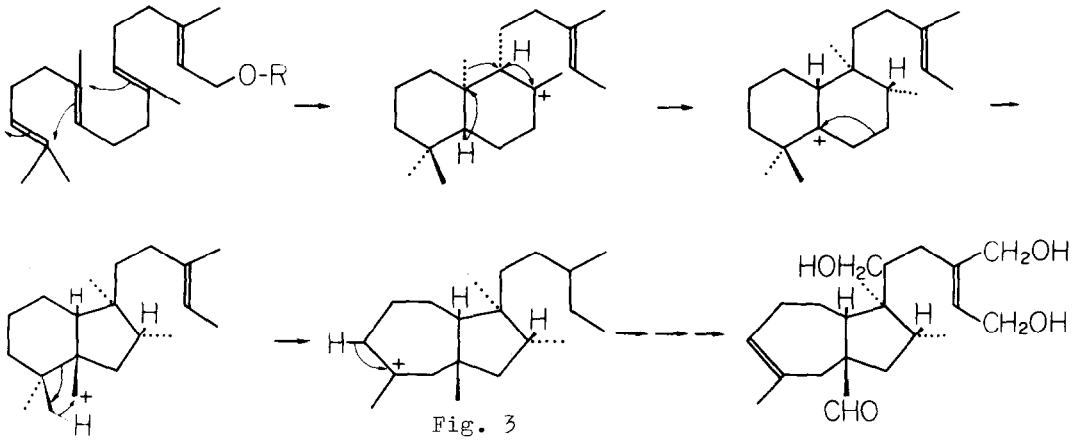


Fig. 3

References

1) The compound was previously called 'portulaca inhibitor' or portulol[2)3)]. The name has been revised as portulal by consent with M. Mitsuhashi et al.

2) M. Mitsuhashi and H. Shibaoka, Plant and Cell Physiol. Japan 6 87 (1965).

3) M. Mitsuhashi, H. Shibaoka and M. Shimokoriyama 1967 Proc. 32nd Ann. Meet. Bot. Soc. Japan p24-25, Kobe.

4) NMR was measured at 60Mc in acetone-d_6 after deuteration. The abbreviations s, d, t and m indicate singlet, doublet, triplet and multiplet, respectively.

5) Refinement is being continued and the full analysis will be published elsewhere.

6) The peripheral numbering system in Fig. 2 is tentatively proposed.

7) Tetracyclic diterpenes containing hydroazulene skeleton have been reported. L. Crombie, M. L. Games and D. J. Pointer, J. Chem. Soc(C) 11 1347 (1968). J. Iwasa, Z. Kumazawa and M. Nakajima, Agr. Biol. Chem. Tokyo 25 782 (1961).