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(+)-ISOBICYCLOGERMACRENAL FROM *ARISTOLOCHIA MANSHURIENSIS*

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Key Word Index—*Aristolochia manshuriensis*; Aristolochiaceae; (+)-isobicyclogermacrenal.

Abstract—The previously unknown (+)-isobicyclogermacrenal was isolated from *Aristolochia manshuriensis*. Its structure was elucidated by spectroscopic means and X-ray analysis.

By separation of the petrol–ether extract (1:1) of the stems of *Aristolochia manshuriensis* Komarov, a crystalline substance (**1**) with mp 54–56° was isolated [1]. The IR, ^{1}H NMR, ^{13}C NMR and mass spectral data are identical with those of (−)-isobicyclogermacrenal (**2**), which was isolated from the liverwort *Lepidozia vitrea* as an oil [2]. Reduction of **1** affords isobicyclogermacrenol (**3**) as does **2**. The optical rotation of **1** is positive; probably it is (+)-isobicyclogermacrenal. However, the rotation value of **1** is twice as high as that of **2** (**1**: $[\alpha]_D^{20}$ + 341° (c = 0.7, $CHCl_3$), **2**: $[\alpha]_D^{20}$ − 168° (c = 1; $CHCl_3$ [2]).

X-Ray diffraction analysis (Fig.1) indicates that **1** must be the (+)-(6*S*,7*R*)-enantiomer of (−)-(6*R*,7*S*)-6,11-cyclogermacra-1(10)*E*,4*E*-dien-14-al, (**2**) [2]. It is interesting to note that in **1** and **3** [2] the C=C double bonds are strongly elongated [1.343(6) and 1.353(6)Å], whereas the C–C single bonds C5–C6 (1.451(6) Å) and C4–C15 (1.451 (6) Å) are likely to be shortened. Furthermore the bonds C1–C2, C3–C4, C9–C10 and C7–C8 are somewhat shortened. Least squares planes calculations for molecule fragments reveal that the planes formed by C5–C6–C7–C8 and C6–C7–C11 intersect an angle of 113°. As expected, the methyl groups C12 and C13 intersect an angle of nearly 90° with the plane formed by atoms C6–C7–C11. The double bonds have identical configurations in **1** and **3**; C1=C10 is established as *trans* and C4=C5 as *cis*.

The 10-membered macro-cyclus (C1–C10) shows nearly the same configuration in both molecules. A list of the torsion angles is given in Table 1. Compounds **1** and **3** only differ in the conformation of the cyclopropane ring (C6–C7–C10) which results in the enantiomeric stereochemistry at atoms C6 and C7.

Crystal data

Compound **1** crystallized orthorhombically with the lattice constants: $a = 8.677(3)$ Å, $b = 11.717(4)$ Å, $c = 13.704(5)$ Å in the space group $p2_12_12_1$. The cell volume was calculated as 1393.3 (8) Å^3, the number of formula units in the elementary cell amounted to $Z = 4$,

Table 1. Torsion angles (°)

	3 [2]	1
C10–C1–C2–C3	94.5	85.3
C2–C1–C10–C15	9.2	9.5
C1–C2–C3–C4	−61.2	−61.6
C2–C3–C4–C5	87.4	89.2
C3–C4–C5–C6	2.3	8.6
C4–C5–C6–C7	−113.4	−117.8
C5–C6–C7–C8	4.0	5.3
C6–C7–C8–C9	90.2	93.3
C7–C8–C9–C10	−69.9	−70.6
C8–C9–C10–C1	89.5	88.4
C9–C10–C1–C2	−163.8	−163.5

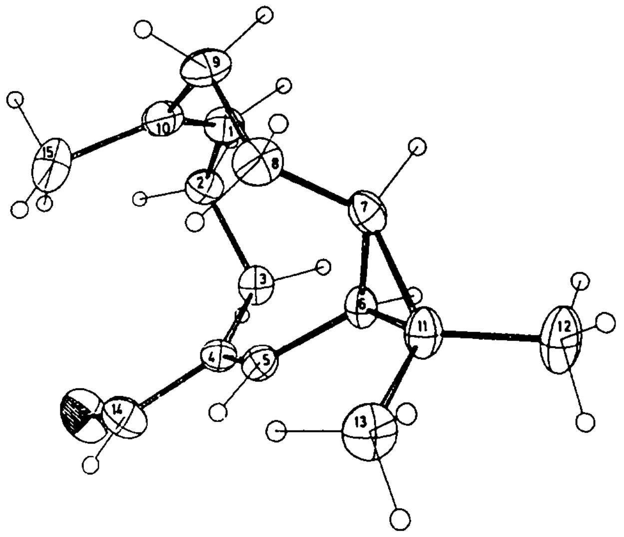
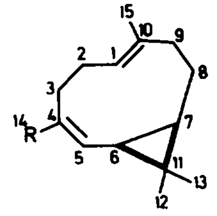


Fig. 1. Molecular structure of (+)-isobicyclogermacrenal (1).



1 R = CHO

3 R = CH_2OH

so that the density was computed to 1.04 g/cm^3. In the region $3^\circ < 2\theta < 54^\circ$2208 reflections (2065 independant reflections) were measured (graphite monochromated MoK-radiation: 0.7107 Å) on an automatic four-circle diffractometer (Nicolet R3m). After correcting (Lorentz and polarisation effects) 1090 structure factors were used for structure elucidation ($F > 4\sigma(F)$). The structure was calculated by Direct Methods (SHELXTL) using full matrix least squares calculations (non-hydrogens unisotropically). The hydrogens were refined isotropically as ideal tetrahedrons. After the final refinement (172 parameters), the R value converged to 0.067 (R_w: 0.051 with $W = 1/\sigma^2$). Scattering factors were used for uncharged atoms (International Tables). Full crystal data of 1 are deposited to the Cambridge Crystallographic Data Centre, University, Chemical Laboratory, Lensfield Road, Cambridge, C82 1EW, U.K.

EXPERIMENTAL

Plant material. The stems of *Aristolochia manshuriensis* were collected in July 1983 in Dae-wha, Kangwon-do province, South Korea. A voucher specimen is deposited at the College of Pharmacy, Seoul, National University.

Extraction and isolation of (+)-(6S,7R)-6,11-*bicyclogermacra*-1(10)E,4E-*dien*-14-*al* (**1**). The dried, powdered stems were repeatedly macerated with petrol-Et_2O (1 : 1). Acids were removed by extraction with 5% Na_2CO_3 soln. The oily residue of the neutral fraction was separated by CC (silica gel 60, methylene chloride). Fractions with R_f 0.45–0.55 (silica gel 60 (Merck), CH_2Cl_2) were separated on silica gel 60 with *n*-hexane–EtOAc (9 : 1). Fractions of this separation with R_f 0.4 (silica gel 60, hexane–EtOAc, 9 : 1) afforded white crystalls, mp 54–56° (*n*-hexane); $[\alpha]_D^{20}$ +341° (c = 0.7; $CHCl_3$). IR, ^{1}H NMR, ^{13}C NMR, MS identical with **2** [2].

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