Urospermal A and Urospermal B, Conformers of a Germacranolide Aldehyde from *Urospermum dalechampii* F. W. Schmidt

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Summary Two crystalline compounds urospermal A and B, isolated from *Urospermum dalechampii*, are interconvertible in solution, and evidence is presented which indicates that they are conformers of the germacranolide aldehyde (II) or its mirror image.

RECENTLY the sesquiterpene dilactone, isabelin (I), has been shown[1] to exist as two conformers at room temperature. A novel germacranolide, urospermal (II), has been isolated from *Urospermum dalechampii* F. W. Schmidt (Liguliflorae) which exists in two interconvertible forms which are considered to be two conformers both stabilised by intramolecular hydrogen-bonding and separable by chromatography to give crystalline solids. It appears that in one conformer (A) hydrogen bonding exists between the aldehyde and the secondary hydroxy-groups and in the other (B) between the primary and secondary hydroxy-groups. Other unusual features of urospermal are the oxidation levels at C-14 and C-15 and the presence of an $\alpha\beta$-unsaturated aldehyde moiety.

Extraction of the minced roots of *Urospermum dalechampii*[2] with either acetone or ether, followed by chromatography of the product, yielded urospermal A and urospermal B. The relative abundance of the two compounds varied according to the polarity of the solvent used for extraction.

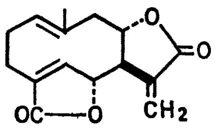
Urospermal A, $C_{15}H_{18}O_5$, m.p. 163—165° (acetone–hexane), $[\alpha]_D$ $-2°$ (Me_2SO) had the following properties: λ_{max} (H_2O) 221 nm ($\log \epsilon$ 3·6), ν_{max} ($CHCl_3$) 1760 cm^{-1} (unsaturated γ-lactone) and 1685 cm^{-1} ($\alpha\beta$-unsaturated aldehyde); n.m.r. spectrum ($[^2H_6]Me_2SO$), τ 0·51 (1H, s, $\cdot CH{=}CR\cdot C\mathit{H}O$), 3·04 (1H, t, J 8 Hz, $\cdot CH_2C\mathit{H}{=}CR\cdot CHO$), 3·70 and 3·96 (2H, m, $=C\mathit{H}_2$ of exocyclic methylene of γ-lactone), 4·40 (1H, d, J 11 Hz $\cdot CH\cdot O\mathit{H}$, signal disappeared on deuterium exchange), 4·91 (1 H, d, J 11 Hz, $R^1R^2C{=}C\mathit{H}\cdot CHR^3\cdot O\cdot CO\cdot$), 5·11 (1 H, 2 overlapping d, J 10 Hz, $>C\mathit{H}\cdot O\cdot CO\cdot$), 5·83 (2H, d, J 5 Hz, $>C{=}CR\,C\mathit{H}_2OH$;

collapsed to a singlet on deuterium exchange), 6·02 (1H, m, *J* 11, 11, 5, and 2, 1 Hz > C*H*·OH; the signal partially collapsed on deuterium exchange *J* 11, 5, and 2 Hz). The remaining 8 protons gave signals between τ 7·2 and 8·2.

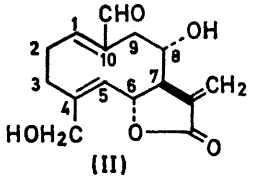
Urospermal B, $C_{15}H_{18}O_5$, m.p. 191—193° (benzene) had the following spectral properties: λ_{max} (H_2O) 218nm (log ϵ 3·7); ν_{max} ($CHCl_3$) 1760 cm^{-1} (unsaturated γ-lactone) and 1685 cm^{-1} ($\alpha\beta$-unsaturated aldehyde); n.m.r. spectrum ([$^2H_6$]Me_2SO), τ 0·51 (1H, s, ·CH=CR·C*HO*), 3·22 (1H, t, *J* 8 Hz, ·CH_2·C*H*=CR·CHO), 3·93 (2H, m, =CH_2 of exocyclic methylene of γ-lactone), 4·73 (1H, d, *J* 6 Hz, >CHO*H*, signal disappeared on deuterium exchange), 4·97 (1H, d, *J* 10 Hz, R^1R^2C=CH·C*H*R^3O·), 5·13 (1H, t, *J* 5 Hz, R·CH_2O*H*), 5·57—5·90 (2H, complex, probably ·CO·O·C*H*< and >C*H*OH; the pattern changes on deuterium exchange), 6·02 and 6·12 (2H, 2 broad singlets $W_{\frac{1}{2}}$ *ca.* 10 Hz, >C=CR·- CH_aH_bOH), 5·9—6·3 (1H, band lies under the singlets at 6·02 and 6·12), 7·0—8·0 (remaining protons).

The mass spectra of the bistrimethylsilyl ether of both compounds indicated the molecular formulae $C_{15}H_{18}O_5$. Both compounds were oxidised by manganese dioxide and were sensitive to acid, base, and heat.

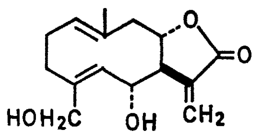
In an attempt to recrystallise urospermal B from acetone–hexane, a conversion in high yield into urospermal A was achieved. When urospermal A was kept in acetone or ethanedithiol at room temperature a mixture of urospermal A and B was obtained. These results can be explained if urospermal A and B are conformers. Recently Cookson, Halton, and Stevens[3] have described the existence of two isolable conformers of cyclotriveratrylen-5-ol.



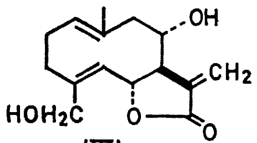
(I)



(II)



(III)



(IV)

The n.m.r. data can be interpreted by structure (II) or its mirror image for urospermal, the stereochemistry at C-6, C-7, and C-8 accounting for the coupling constants of the protons at C-6 and C-8. This stereochemistry is identical with that found in artemisiifolin (III),[1,4] the related compound cnicin,[5] and salonitenolide (IV)[6] which differs from structure (II) only in possessing a methyl group instead of an aldehyde group. In urospermal A the large coupling constant (*J* 11 Hz) for the C-6 hydroxy-proton suggests that it is strongly hydrogen-bonded. In this conformer, only this hydroxy-proton is at low field (τ 4·40). In urospermal B, both hydroxy-protons have significant coupling constants and give signals at low field (τ 4·73 and 5·13) and the two protons on the carbon of the CH_2OH group are no longer magnetically equivalent. An explanation of these observations is that in urospermal A the C-6 hydroxy-group is hydrogen-bonded to the aldehyde group and in urospermal B it is involved in hydrogen bonding with the CH_2OH group. This is possible with the stereochemistry of structure (II). The most likely conformer corresponding to urospermal A is the one with the aldehyde group "*cis*" to the C-8 hydroxy-group and the C-5 proton and the CH_2OH group "*trans*" to the C-8 hydroxy-group. In the one corresponding to urospermal B, both double bonds have probably rotated, leading to the aldehyde group being "*cis*" to the C-5 proton and "*trans*" to the C-8 hydroxy-group which is now "*cis*" to the CH_2OH group. This conformer corresponds to conformer (Ib) for isabelin in Mabry's paper.[1] The further examination of urospermal is in progress.

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[1] H. Yoshioka, T. J. Mabry, and H. E. Miller, *Chem. Comm.*, 1968, 1679.
[2] R. K. Bentley, Sir Ewart R. H. Jones, and V. Thaller, *J. Chem. Soc.* (*C*), 1969, 1096.
[3] R. C. Cookson, B. Halton, and I. D. R. Stevens, *J. Chem. Soc.* (*B*), 1968, 767.
[4] T. H. Porter, T. J. Mabry, H. Yoshioka, and N. H. Fischer, *Phytochemistry*, 1970, **9**, 199.
[5] Z. Samek, M. Holub, V. Herout, and F. Šorm, *Tetrahedron Letters*, 1969, 2931.
[6] H. Yoshioka, W. Renold, and T.J. Mabry, *Chem. Comm.*, 1970, 148.