# SESQUITERPENE LACTONES OF *Urospermum dalechampii* SCHMIDT*

Urszula RYCHLEWSKA[a], Derek J. HODGSON[b], Halina GRABARCZYK[c], Bohdan DROŻDŻ[c], Włodzimierz M. DANIEWSKI[d], Wojciech KROSZCZYŃSKI[d], Miloš BUDĚŠÍNSKÝ[e] and Miroslav HOLUB[e]

[a] *Laboratory of Crystallography, Department of Chemistry, Adam Mickiewicz University, Poznań, Poland,*
[b] *Department of Chemistry, University of North Carolina, Chapel Hill, N.C. 27514, U.S.A.,*
[c] *Department of Medicinal Plants, Academy of Medicine, 60—623 Poznań, Poland,*
[d] *Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland and*
[e] *Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Prague, Czechoslovakia*

Received October 24th, 1985

In the species *Urospermum dalechampii* SCHMIDT urospermal A (*I*) and 11βH,13-dihydrourospermal A (*II*) were detected. The latter compound was also detected in *U. picroides* SCHMIDT. The spectral characteristics of both lactones were completed by $^{13}C$ NMR data. The structure of 11βH,13-dihydrourospermal A (*II*) was also confirmed by X-ray analysis.

In connection with a systematic study of sesquiterpenic lactones we also investigated the species *Urospermum dalechampii* SCHMIDT (*Compositae* family, *Cichorieae* tribe) from which we isolated urospermal A (*I*) and 11βH,13-dihydrourospermal A (*II*).

Urospermal A (*I*) was already obtained earlier from *U. picroides* SCHMIDT[1], while the glucoside of urospermal A (*III*, ref.[2]) and *p*-hydroxyphenylacetate of the glucoside of urospermal A (*IV*) were obtained later from the same plant material[3]. Urospermal (*I*) and 11βH,13-dihydrourospermal A (*II*) were also found in the species *Dicoma tomentosa* CASS. (*Compositae* family, *Mutisieae* tribe)[4]. For comparison we isolated urospermal A (*I*) from *U. picroides* and we succeeded in detecting 11βH,13-dihydrourospermal A in this material for the first time.

The sesquiterpene lactone urospermal A was originally described[1] as a mixture of conformers, each containing the *trans,trans* (germacrolide) structure *V*, and although the NMR spectrum has been interpreted[2-4] more recently as indicating that the double bond 1,10 is *cis*, giving rise to the *cis,trans* (melampolide) structure *I*,

* Part CCXCIII in the series On Terpenes; Part CCXCII.: Phytochemistry, in press.

the original assignment remains firmly entrenched in the literature[5]. Consequently, it was desirable to determine the crystal structure of this molecule or a suitable derivative, so that the assignment of the geometry of the ten-membered ring could be made with certainty. We report here the crystal structure of 11βH,13-dihydrourospermal A (*II*).

The structure of 11βH,13-dihydrourospermal A (*I*) is shown in Fig. 1. The atomic positional parameters are listed in Table I, bond lengths and angles in Table II and III, respectively, and torsion angles in Table IV. The compound *II* is a melampolide sesquiterpene lactone; consequently, the correct structural assignment for the parent compound urospermal A is established as *I*, in which the 1,10 double bond is *cis*. The cyclodecadiene ring is ***trans*** fused at C(6)—C(7) to the γ-lactone. The ten-membered ring adopts a distorted chair-boat conformation which is typical of melampolides[6-11]. As has been observed in the majority of melampolides the structures of which have been determined crystallographically[6-11], the substituents at C(4) and C(10) are *anti*, with the aldehyde group at C(10) pseudo-α and the primary alcohol at C(4) pseudo-β. The torsion angles in the cyclodecadiene ring (listed in Table IV) are very similar to those observed in the closely related compound alloschkuhriolide (*VI*) in which the only major difference is that the hydroxyl group at C(8) is β, while in 11βH,13-dihydrourospermal (*II*) it is α. The γ-lactone, as expected, adopts the 7α-envelope conformation[12].

As predicted from the original NMR study[1], the conformation observed has the hydroxyl group O(3)H *cis* to the aldehyde group at C(10) (both are α), while the

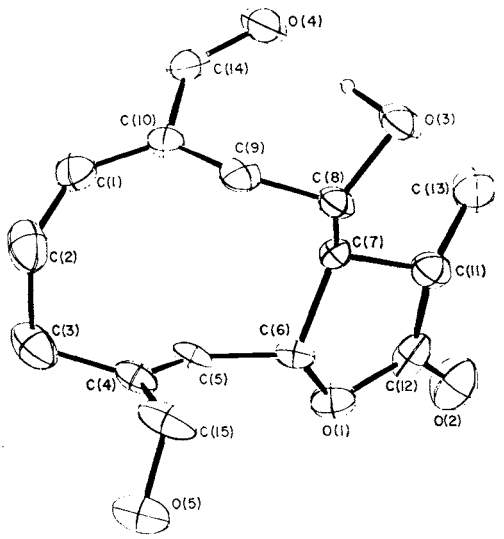



FIG. 1

View of one molecule of 11,13-dihydrourospermal A (*II*). Thermal ellipsoids are drawn at the 25% probability level; hydrogen atom H(O3) is shown as a sphere of arbitrary size, and other hydrogen atoms are omitted for clarity

TABLE I

Atomic positional parameters for *II*

| Atom | *X* | *Y* | *Z* |
|---|---|---|---|
| O(1) | −0·1436(3) | −0·0809(2) | −0·5558(5) |
| O(2) | −0·0218(3) | 0·0195(3) | −0·6353(7) |
| O(3) | −0·2614(3) | −0·1386(3) | −1·1306(5) |
| O(4) | −0·1240(3) | −0·2810(3) | −1·1504(5) |
| O(5) | −0·4647(3) | −0·2170(3) | −0·3224(5) |
| C(1) | −0·2458(5) | −0·3907(4) | −0·7996(8) |
| C(2) | −0·3330(6) | −0·4075(4) | −0·6624(10) |
| C(3) | −0·3097(5) | −0·3628(5) | −0·4853(9) |
| C(4) | −0·3163(4) | −0·2655(4) | −0·5094(7) |
| C(5) | −0·2298(4) | −0·2209(4) | −0·5585(6) |
| C(6) | −0·2266(4) | −0·1350(3) | −0·6383(7) |
| C(7) | −0·1907(4) | −0·1382(3) | −0·8310(7) |
| C(8) | −0·2872(4) | −0·1623(4) | −0·9538(7) |
| C(9) | −0·3257(4) | −0·2560(4) | −0·9438(7) |
| C(10) | −0·2410(5) | −0·3260(3) | −0·9182(7) |
| C(11) | −0·1391(4) | −0·0497(4) | −0·8555(8) |
| C(12) | −0·0933(4) | −0·0304(3) | −0·6763(10) |
| C(13) | −0·0492(5) | −0·0406(4) | −0·9949(10) |
| C(14) | −0·1437(5) | −0·3310(4) | −1·0326(8) |
| C(15) | −0·4292(5) | −0·2288(5) | −0·4956(9) |
| H(03) | −0·205(4) | −0·192(3) | −1·135(8) |
| H(1) | −0·186(0) | −0·431(0) | −0·803(0) |
| H(2) | −0·401(0) | −0·388(0) | −0·708(0) |
| H(2′) | −0·337(0) | −0·470(0) | −0·646(0) |
| H(3) | −0·362(0) | −0·381(0) | −0·402(0) |
| H(3′) | −0·238(0) | −0·379(0) | −0·466(0) |
| H(5) | −0·160(0) | −0·247(0) | −0·540(0) |
| H(6) | −0·299(0) | −0·112(0) | −0·627(0) |
| H(7) | −0·141(0) | −0·183(0) | −0·862(0) |
| H(8) | −0·348(0) | −0·129(0) | −0·917(0) |
| H(9) | −0·375(0) | −0·259(0) | −0·847(0) |
| H(9′) | −0·363(0) | −0·269(0) | −1·049(0) |
| H(11) | −0·193(0) | −0·011(0) | −0·898(0) |
| H(13) | −0·023(0) | 0·017(0) | −0·997(0) |
| H(13′) | −0·078(0) | −0·056(0) | −1·106(0) |
| H(13″) | 0·010(0) | −0·080(0) | −0·967(0) |
| H(14) | −0·093(0) | −0·377(0) | −1·012(0) |
| H(15) | −0·430(0) | −0·172(0) | −0·552(0) |
| H(15′) | −0·479(0) | −0·266(0) | −0·553(0) |

$CH_2OH$ group at C(4) is *trans* to the proton at C(5) (pseudo-β and α, respectively). The pseudo-*cis* conformation (α, α), of the substituents at C(8) and C(10) permits the formation of a strong intramolecular hydrogen bond, the O(3)...O(4) and

TABLE II
Bond lengths (Å)

| Bond | Distance | Bond | Distance |
|---|---|---|---|
| C(1)—C(2) | 1·514(7) | C(8)—C(9) | 1·510(6) |
| C(1)—C(10) | 1·343(6) | C(8)—O(3) | 1·433(5) |
| C(2)—C(3) | 1·542(7) | C(9)—C(10) | 1·501(6) |
| C(3)—C(4) | 1·501(7) | C(10)—C(14) | 1·475(7) |
| C(4)—C(5) | 1·312(5) | C(11)—C(12) | 1·507(7) |
| C(4)—C(15) | 1·489(6) | C(11)—C(13) | 1·534(6) |
| C(5)—C(6) | 1·449(6) | C(12)—O(1) | 1·348(5) |
| C(6)—C(7) | 1·537(6) | C(12)—O(2) | 1·200(5) |
| C(6)—O(1) | 1·451(4) | C(14)—O(4) | 1·205(5) |
| C(7)—C(8) | 1·548(5) | C(15)—O(5) | 1·404(5) |
| C(7)—C(11) | 1·505(5) | | |

TABLE III
Bond angles (deg)

| Atoms | Angle | Atoms | Angle |
|---|---|---|---|
| C(2)—C(1)—C(10) | 128·5(5) | C(9)—C(8)—O(3) | 110·8(4) |
| C(1)—C(2)—C(3) | 113·7(4) | C(8)—C(9)—C(10) | 118·0(4) |
| C(2)—C(3)—C(4) | 108·8(4) | C(1)—C(10)—C(9) | 125·7(5) |
| C(3)—C(4)—C(5) | 120·5(4) | C(1)—C(10)—C(14) | 113·4(5) |
| C(3)—C(4)—C(15) | 114·5(4) | C(9)—C(10)—C(14) | 120·9(4) |
| C(5)—C(4)—C(15) | 124·5(4) | C(7)—C(11)—C(12) | 102·6(4) |
| C(4)—C(5)—C(6) | 127·9(4) | C(7)—C(11)—C(13) | 117·7(4) |
| C(5)—C(6)—C(7) | 112·4(3) | C(12)—C(11)—C(13) | 110·4(4) |
| C(5)—C(6)—O(1) | 110·7(3) | C(11)—C(12)—O(1) | 109·9(4) |
| C(7)—C(6)—O(1) | 103·6(3) | C(11)—C(12)—O(2) | 129·0(6) |
| C(6)—C(7)—C(8) | 111·8(3) | O(1)—C(12)—O(2) | 121·0(6) |
| C(6)—C(7)—C(11) | 102·1(3) | C(10)—C(14)—O(4) | 124·7(5) |
| C(8)—C(7)—C(11) | 117·2(3) | C(4)—C(15)—O(5) | 113·6(4) |
| C(7)—C(8)—C(9) | 115·6(3) | C(6)—O(1)—C(12) | 110·3(3) |
| C(7)—C(8)—O(3) | 110·1(3) | | |

TABLE IV
Torsion angles (deg)

| Atom 1 | Atom 2 | Atom 3 | Atom 4 | Angle |
|---|---|---|---|---|
| C(10) | C(1) | C(2) | C(3) | −90·5 |
| C(1) | C(2) | C(3) | C(4) | 66·6 |
| C(2) | C(3) | C(4) | C(5) | −87·5 |
| C(3) | C(4) | C(5) | C(6) | 159·5 |
| C(4) | C(5) | C(6) | C(7) | −110·2 |
| C(5) | C(6) | C(7) | C(8) | 81·7 |
| C(6) | C(7) | C(8) | C(9) | −71·4 |
| C(7) | C(8) | C(9) | C(10) | −37·2 |
| C(8) | C(9) | C(10) | C(1) | 131·3 |
| C(9) | C(10) | C(1) | C(2) | −2·0 |
| C(6) | C(7) | C(11) | C(12) | 31·2 |
| C(7) | C(11) | C(12) | O(1) | −19·7 |
| C(11) | C(12) | O(1) | C(6) | −1·5 |
| C(12) | O(1) | C(6) | C(7) | 21·7 |
| O(1) | C(6) | C(7) | C(11) | −32·6 |
| C(2) | C(3) | C(4) | C(15) | 85·1 |
| C(3) | C(4) | C(15) | O(5) | 80·5 |
| C(5) | C(4) | C(15) | O(5) | −107·2 |
| C(15) | C(4) | C(5) | C(6) | −12·3 |
| C(4) | C(5) | C(6) | O(1) | 134·4 |
| O(1) | C(6) | C(7) | C(8) | −158·7 |
| C(5) | C(6) | C(7) | C(11) | −152·2 |
| C(6) | C(7) | C(8) | O(3) | 162·1 |
| C(11) | C(7) | C(8) | C(9) | 171·3 |
| C(11) | C(7) | C(8) | O(3) | 44·8 |
| O(3) | C(8) | C(9) | C(10) | 89·0 |
| C(8) | C(9) | C(10) | C(14) | −51·5 |
| C(14) | C(10) | C(1) | C(2) | −179·4 |
| C(9) | C(10) | C(14) | O(4) | 0·7 |
| C(1) | C(10) | C(14) | O(4) | 178·3 |
| C(6) | C(7) | C(11) | C(13) | 152·6 |
| C(8) | C(7) | C(11) | C(12) | 153·7 |
| C(8) | C(7) | C(11) | C(13) | −84·9 |
| C(7) | C(11) | C(12) | O(2) | 158·7 |
| C(13) | C(11) | C(12) | O(1) | −146·0 |
| C(13) | C(11) | C(12) | O(2) | 32·4 |
| O(2) | C(12) | O(1) | C(6) | 179·9 |
| C(12) | O(1) | C(6) | C(5) | 142·5 |

TABLE V

Proton NMR parameters of compounds *I*, *II*, *VII*, and *VIII*

| Proton | Chemical shifts | | | | | |
|---|---|---|---|---|---|---|
| | *I* | *VII* | $\Delta\delta^a$ | *II* | *VIII* | $\Delta\delta^a$ |
| H(1) | 6·84 ddd | 6·70 | −0·14 | 6·81 ddd | 6·65 | −0·16 |
| H(2) | [b] | [b] | [b] | [b] | [b] | [b] |
| H(2′) | [b] | [b] | [b] | [b] | [b] | [b] |
| H(3) | 2·77 ddd | 2·70 | −0·07 | 2·74 ddd | [b] | [b] |
| H(3′) | 2·01 bdt | 2·21 | 0·20 | 1·99 bdt | 2·19 | 0·20 |
| H(5) | 5·09 dq | 5·41 | 0·32 | 5·02 dq | 5·32 | 0·30 |
| H(6) | 4·73 dd | 4·85 | 0·12 | 4·76 dd | 4·87 | 0·11 |
| H(7) | 2·46 tt | 2·88 | 0·42 | 1·58 m | 1·95 | 0·37 |
| H(8) | 3·99 dddd | 5·30 | 1·31 | 3·83 m | 5·24 | 1·41 |
| H(9) | 2·70 bdd | 3·01 | 0·31 | 2·69 bdd | 2·82 | 0·13 |
| H(9′) | 2·45 bdd | 2·43 | −0·02 | [b] | [b] | [b] |
| H(13) | 6·52 dd | 5·82 | −0·70 | 1·39 d | 1·31 | −0·08 |
| H(13′) | 6·30 dd | 6·30 | 0·00 | — | — | — |
| H(14) | 9·46 d | 9·53 | 0·07 | 9·45 d | 9·55 | 0·10 |
| H(15) | 4·36 bd | 5·02 | 0·66 | 4·39 dd | 5·01 | 0·62 |
| H(15′) | | | | 4·30 dd | | 0·71 |
| OH(8) | 5·73 d | — | — | 5·30 d | — | — |
| OH(15) | 2·24 t | — | — | 2·50 t | — | — |
| NH | — | 8·69 | — | — | 8·75 | — |
| | — | 8·93 | — | — | 8·70 | — |

Coupling constants

| $H_i$, $H_j$ | *I* | *II* | $H_i$, $H_j$ | *I* | *II* |
|---|---|---|---|---|---|
| (1, 2) | 9·8 | 9·6 | (7, 8) | 10·6 | 10·6 |
| (1, 2′) | 7·7 | 7·9 | (7, 13) | 3·0 | 0 |
| (1, 9) | 1·8 | 1·8 | (7, 13′) | 3·3 | 0 |
| (2, 2′) | [b] | [b] | (7, 11) | — | 11·4 |
| (2, 3) | 2·4 | 2·5 | (8, 9) | 5·0 | 5·4 |
| (2, 3′) | 12·1 | 12·0 | (8, 9′) | 1·9 | 1·7 |
| (2′, 3) | 5·6 | 5·4 | (8, OH) | 11·2 | 11·5 |
| (2′, 3′) | 3·0 | 3·6 | (9, 9′) | 16·0 | 16·0 |
| (3, 3′) | 12·4 | 12·0 | (9′, 14) | 1·3 | 1·3 |
| (3′, 5) | 0·8 | 0·8 | (11, 13) | — | 7·0 |
| (5, 6) | 10·7 | 10·7 | (15,15′) | [b] | 13·0 |
| (5, 15) | 0·8 | 0·8 | (15, OH) | 4·6 | 4·0; 5·4 |
| (6, 7) | 9·5 | 9·8 | | | |

[a] Trichloroacetyl isocyanate induced acylation shifts; [b] not determined.

H(03)...O(4) distances and O(3)—H(03)...O(4) angle being 2·751(5), 1·69(6) Å* and 175(5)°, respectively. The β configuration of the OH group at C(8) precludes such an interaction in alloschkuhriolide (*VI*). There is no compelling evidence for hydrogen bonding involving O(5). This atom approaches atom O(3) of a symmetry-related molecule at a distance of 3·118(5) Å, which indicates that any interaction between the two atoms must be weak. Moreover, our failure to locate the hydrogen atom associated with this hydroxyl group strongly suggests that it is not involved in any significant interaction and is consequently relatively unrestrained.

We also investigated urospermal A (*I*) and 11βH,13-dihydrourospermal A (*II*) in detail by means of $^1$H and $^{13}$C NMR spectroscopy. The NMR data obtained (see Tables V and VI) are fully consistent with the structures *I* and *II* and with the results of X-ray analysis of compound *II*. Very similar chemical shift values of hydrogen and carbon atoms in analogous positions and of the coupling constants of hydrogen atoms indicated the same conformational arrangement of both substances. The high value of the vicinal coupling of the C(8)—OH hydrogen ($J_{8,OH} \approx \approx 11{\cdot}5$ Hz) shows that in solution too there is a strong intramolecular H-bridge C(8)—OH to the aldehydic oxygen atom, leading to a stabilization of the antiperi-

TABLE VI

$^{13}$C NMR parameters of compounds *I*, *II*, *VII*, and *VIII*

| Carbon | *I* | *VII* | $\Delta\delta^a$ | *II* | *VIII* | $\Delta\delta^a$ |
|---|---|---|---|---|---|---|
| C(1) | 160·34 | 153·84 | −6·50 | 159·49 | 153·53 | −5·96 |
| C(2) | 27·83 | 27·68 | −0·15 | 27·66 | 27·77 | 0·11 |
| C(3) | 32·75 | 32·43 | −0·32 | 32·70 | 32·54 | 0·16 |
| C(4) | 141·55 | 135·35 | −6·20 | 140·56 | 135·28 | −5·28 |
| C(5) | 126·71 | 129·86 | 3·15 | 127·51 | 130·03 | 2·52 |
| C(6) | 75·78 | 75·42 | −0·36 | 75·86 | 75·47 | −0·39 |
| C(7) | 51·54 | 48·45 | −3·09 | 55·94 | 48·56 | −7·38 |
| C(8) | 69·98 | 74·64 | 4·66 | 71·34 | 74·63 | 3·29 |
| C(9) | 33·10 | 28·21 | −4·89 | 33·06 | 28·29 | −4·77 |
| C(10) | 144·20 | 142·91 | −1·29 | 144·50 | 143·04 | −1·46 |
| C(11) | 136·90 | 137·51 | 0·61 | 41·20 | 41·29 | 0·09 |
| C(12) | 175·25 | *b* | *b* | 179·42 | *b* | *b* |
| C(13) | 125·12 | 124·24 | −0·88 | 16·27 | 17·57 | 1·30 |
| C(14) | 199·64 | 194·31 | −5·33 | 199·46 | 194·23 | −5·23 |
| C(15) | 61·02 | 64·61 | 3·59 | 60·75 | 64·78 | 4·03 |

[a] Trichloroacetyl isocyanate induced acylation shifts; [b] not determined.

* 1 Å = $10^{-10}$ m.

planar orientation of the hydrogen atoms H—C(8)—OH. In contrast to this the equal or very close chemical shifts of both hydrogen atoms of the primary C(15)--alcoholic group in *I* or *II*, together with the values $J_{15,OH} \approx 5$ Hz, indicate a flexibility of the —$CH_2OH$ group and exclude a more pronounced participation of this hydroxyl in the intramolecular H-bridge. Using *in situ* acylation with trichloroacetyl isocyanate (TAI)[13,14] in the NMR cell compounds *I* and *II* were converted to corresponding bis(trichloroacetylcarbamoyl) derivatives *VII* and *VIII*, again characterized by $^1$H and $^{13}$C NMR spectra (Tables V and VI). In their $^1$H NMR spectra interesting upfield shifts of the hydrogens H(13) (−0·70 ppm in *I*) and H(1) (about −0·15 ppm in *I* and *II*) were observed in addition to the expected distinct downfield acylation shifts of α-hydrogens (about 1·35 or 0·65 ppm for H(8) or H(15), respectively), as well as the disappearance of the geminal coupling $J_{13,13'}$ in derivative *VII*, caused by the acylation of the C(8)—OH group. This also becomes manifest through distinct effects in the $^{13}$C NMR spectra where in addition to the expected acylation shifts of carbon atoms in the neighbourhood of the OH group a distinct affecting of the carbons C(14), C(10), and C(1) is also observed ($\Delta\delta$ −6·0; −1·5 or +3·0 ppm in *I* or *II*, respectively), evidently in consequence of the abolition of the intramolecular H-bridge of C(8)—OH.

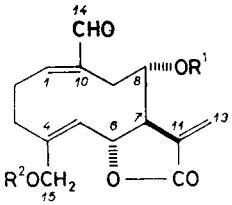
TABLE VII

Comparison of X-ray and $^1$H NMR conformational data of 11βH,13-dihydrourospermal A (*II*)

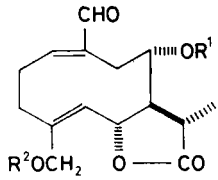
| $H_i$, $H_j$ | $\Phi_{i,j}$(X-ray)[a] | $J_{i,j}$ | $\Phi_{i,j}$(NMR)[b] |
|---|---|---|---|
| 1, 2 | −149 | 9·6 | 150 |
| 1, 2′ | −32 | 7·9 | 30 |
| 2, 3 | 66 | 2·5 | 65 |
| 2, 3′ | −175 | 12·0 | 165 |
| 2′, 3 | −54 | 5·4 | 45 |
| 2′, 3′ | 66 | 3·6 | 55 |
| 5, 6 | −169 | 10·7 | 160 |
| 6,7 | −149 | 9·8 | 155 |
| 7, 8 | 168 | 10·6 | 160 |
| 8, 9 | −34 | 5·4 | 45 |
| 8, 9′ | 84 | 1·7 | 70 |
| 7, 11 | 143 | 11·4 | 160 |

[a] Hydrogen atoms are in calculated positions (see text); [b] determined from $J_{i,j}$ using Karplus-like relation[15]; only absolute values of the angles are obtainable; from two possible angles (corresponding to *J* value due to the periodicity of Karplus curve) only one, which is closer to $\Phi_{i,j}$ (X-ray), is given (rounded off to nearest five degrees).

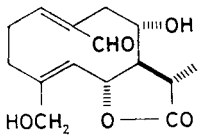
We further tried to make a more detailed comparison of the conformation of compound *II* in the crystal and in solution. From the X-ray data (Table IV) we calculated approximate values of torsion angles of hydrogen atoms, characterizing the conformation of compound *II* in a crystal. From the values of the $^3J_{H,H}$ coupling



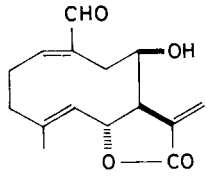

*I*, $R^1 = R^2 = H$
*III*, $R^1 = H$; $R^2$ = Gluc
*IV*, $R^1 = H$; $R^2$ = Gluc-HPA
*VII*, $R^1 = R^2$ = Tac




*II*, $R^1 = R^2 = H$
*VIII*, $R^1 = R^2$ = Tac




*V*




*VI*

In formulae : Gluc = glucosyl,
Gluc-HPA = glucosyl—$OCOCH_2C_6H_4OH(p)$,
Tac = $CONHCOCCl_3$

constants in the $^1$H NMR spectrum of compound *II* we calculated – using the Karplus-like relation[15] – the approximate torsion angles of hydrogen atoms, characterizing the conformation in solution. The results summarized in Table VII show very similar torsion angle values, obtained by both approaches. From this it follows that compound *II* assumes the same conformation in solution as was found in crystal. This conformation also fulfils the geometric conditions for the observed long-range interactions $^4J_{H,H}$: *a*) four-bond-coupling $^4J_{9',14} = 1{\cdot}3$ Hz (an almost planar zig-zag arrangement of the H(9')—C(9)—C(10)—C(14)—H(14) fragment; *b*) allylic couplings $^4J_{1,9} = 1{\cdot}8$ Hz and $^4J_{1,14} \approx 0$ Hz (torsion angles $\Phi$ (H(9), C(1)) $\approx 120°$ or $\Phi$ (H(14), C(1)) $\approx 0°$, respectively).

## EXPERIMENTAL

The melting points were determined on a Kofler block and they are not corrected. Silica gel for column chromatography was prepared according to Pitra and Štěrba (30–60 mμ, deactivated by addition of 11% of water). Thin-layer chromatography was carried out on silica gel G (Merck) according to Stahl. The IR spectra were measured in chloroform, unless stated otherwise, using a Perkin–Elmer PE 580 spectrophotometer. The NMR spectra were measured on a FT NMR spectrometer Varian XL-200 ($^1$H on a 200 MHz and $^{13}$C on a 50·3 MHz frequency). The spectra of compounds *I* and *II* were measured in deuteriochloroform using tetramethylsilane as internal reference, the spectra of bis(trichloroacetylcarbamoyl) derivatives *VII* and *VIII* were obtained by addition of a mild excess of trichloroacetyl isocyanate to solutions of compounds *I* and *II* in the NMR cell. "Attached proton test" pulse sequence[16] was applied for the determination of directly bound hydrogens in the $^{13}$C NMR spectra. The mass spectra were measured on an AEI MS 902 spectrometer, optical rotations were measured on an objective Perkin–Elmer 141 polarimeter in methanol. CD was measured on a Roussel Jouan CD 185 dichrographe.

### Isolation of Sesquiterpenic Lactones from *U. dalechampii*

Fresh aerial part (3·5 kg) (voucher RL 469/82 is deposited in the herbarium of the Zaklad Roślin Leczniczych, Akademia Medyczna, Poznań, Poland) was processed in the described manner[17], affording the so-called lactone fraction (7·8 g). A part of this fraction (2 g) was filtered through a layer of silica gel, using chloroform–2-propanol (19 : 1) mixture and then chromatographed on silica gel (285 g, 230–400 mesh) under pressure 500 kPa, using a mixture of chloroform and increasing proportion of 2-propanol (up to 10%) for elution. Five fractions were thus obtained, of which the medium one (560 mg) was rechromatographed under medium pressure using a series of 3 HPLC columns (25 × 400 mm) filled with silica gel (40–60 μ) and a chloroform–2-propanol 1–5% gradient solvent system (flow rate 5 ml/min). It afforded 11βH,13-dihydrourospermal A (*II*; 70 mg), m.p. 178–180°C. IR spectrum (in cm$^{-1}$): 3 615, 3 420 (hydroxyl), 1 769 (γ-lactone), 1 671 (α,β-unsaturated aldehyde), 1 619 (double bond). Mass spectrum (*m/z*): 280 (M), 262 (M – 18), 249, 244 (M – 18 – 18), 233, 216, 189, 171, 159, 152, 82. CD spectrum (nm, Δε): 319, +2·8; 274, ±0; 230, −18·7. For $C_{15}H_{20}O_5$ (280·3) calculated: 64·27% C, 7·19% H, 0·71% H act.; found: 64·09% C, 7·28% H, 0·92% H act. The most polar fraction (400 mg) was submitted to similar chromatography as above, affording urospermal A (*I*; 45 mg), m.p. 168–170°C. IR spectrum (cm$^{-1}$) (in KBr): 3 367, 3 278 (hydroxyl), 1 756 (γ-lactone), 1 658 (α,β-unsaturated aldehyde), 1 614 (double bond). Mass spectrum (*m/z*): 278 (M), 260 (M – 18), 247 (M – $CH_2OH$), 242 (M – 18 – 18), 231, 214, 213, 69, 41. CD spectrum (nm, Δε): 317, +2·2; 280, ±0; 248, −7·6; 224, ±0; 205, +19·4 (last reading). For $C_{15}H_{18}O_5$ (278·3) calculated: 64·73% C, 6·52% H, 0·72% H act.; found: 64·59% C, 6·73% H, 0·86% H act.

### Isolation of Sesquiterpenic Lactones from *U. picroides*

Fresh aerial part (1·7 kg) (voucher RL 40/81 is deposited in the herbarium of Zaklad Roślin Leczniczych, Akademia Medyczna, Poznań, Poland) of the plant was processed as described in ref.[17] and the so-called lactone fraction was thus obtained (5 g). A part of this fraction (4·5 g) was chromatographed on silica gel (150 g) with benzene containing ethyl acetate (from 5 to 20%) and then with ether with increasing amount of methanol (from 1 to 50%). From the more polar fraction (100 mg) 11βH,13-dihydrourospermal A (*II*; 35 mg) was obtained, melting at 177–179°C (from ethyl acetate–methanol). According to IR and $^1$H NMR spectra and mixture melting point it was identical with a similar compound obtained from *U. dalechampii*. A further, more polar fraction (150 mg) was dissolved in a mixture of chloroform with 5% 2-propanol and was filtered

through silica gel and chromatographed under pressure (500 kPa) as mentioned in the description of the isolation of urospermal A from *U. dalechampii*. Urospermal A (*I*; 30 mg) was thus obtained with m.p. 167–170°C which according to mixture melting point and IR and $^1$H NMR spectra was identical with the substance isolated from *U. dalechampii*.

X-ray Structural Analysis of 11βH,13-Dihydrourospermal A (*II*)

Crystal Data: $C_{15}H_{20}O_5$. Orthorhombic, $P2_12_12_1$, $a = 12{\cdot}184(4)$, $b = 15{\cdot}296(5)$, $c = 7{\cdot}639(5)$ Å. $U = 1\,424(2)$ Å$^3$, $Z = 4$, $D_m = 1{\cdot}28$, $D_c = 1{\cdot}31$ g cm$^{-3}$, $T = 295$ K.

Data Collection: Suitable crystals were grown from a mixture of acetone and n-pentane; a crystal of dimensions 0·4 × 0·6 × 1·0 mm was used for data collection in Chapel Hill on an Enraf–Nonius CAD4 diffractometer equipped with a molybdenum tube ($\lambda K_\alpha = 0{\cdot}7107$ Å) and a graphite monochromator. Cell constants were obtained by a least squares refinement of the positions of 25 reflections with $22° < 2\Theta(\mathrm{Mo}) < 38°$. 1 791 independent intensities were gathered in a $\omega$-2$\Theta$ scan mode in the region $2° \leqq 2\Theta(\mathrm{Mo}) \leqq 54°$; there was very little observable diffracted intensity at values of $2\Theta(\mathrm{Mo}) > 54°$. The data were corrected for background and for Lorentz-polarization effects, but not for absorption, and assigned estimated standard deviations using the method of Ibers and coworkers[18] with $p = 0{\cdot}02$. Of the 1 791 independent data, only 906 reflections had $I > \sigma(I)$, and only these data were used in the subsequent structure refinement.

Solution and Refinement of the Structure: The structure was solved by direct methods[19] and refinement by full-matrix least-squares techniques. All refinements were carried out on $F$, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$, where the weights $w$ are defined as $4F_o^2/\sigma^2(F_o^2)$. The hydrogen atoms attached to carbon atoms were placed in calculated positions assuming C—H distances of 0·95 Å, and these positions were not refined. The hydrogen atom on the secondary hydroxyl group O(3)H was located in a difference Fourier map and was refined isotropically, but the hydrogen atom associated with the primary hydroxyl group O(5)H could not be located; all other atoms were refined anisotropically. The final values of the agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ were 0·069 and 0·056, respectively, and the error in an observation of unit weight was 2·1. In the final least-squares cycle no parameter experienced a shift of more than $0{\cdot}2\sigma$ which indicates convergence. A final difference Fourier map was featureless, with no peak higher than 0·11 e Å$^{-3}$. The final positional parameters, along with their standard deviations as estimated from the inverse matrix, are collected in Table I. Tables of anisotropic thermal parameters and observed and calculated structure amplitudes are available on request (D.J.H.). The positions in Table I and elsewhere were assigned on the assumption of the established configuration at C(7).

REFERENCES

1. Bentley R. K., Buchanan J. G. S., Halsall T. G., Thaller V.: J. Chem. Soc., Chem. Commun. *1970*, 435.
2. Amer M. M. A., Salama O. M., Bohlmann F., Ziesche J.: Phytochemistry *23*, 692 (1984).
3. Salam N. A. A., Mahmoud Z. F., Ziesche J., Bohlmann F.: Phytochemistry *21*, 2746 (1982).
4. Bohlmann F., Singh P., Jakupovic J.: Phytochemistry *21*, 2122 (1982).
5. Seaman F. C.: Botanic. Rev. *48*, 121 (1982).
6. Kartha G., Go K. T., Joshi B. S.: J. Chem. Soc., Chem. Commun. *1972*, 1327.
7. Watkins S. F., Fisher N. H., Bernal I.: Proc. Natl. Acad. Sci. U.S.A. *70*, 2434 (1973).
8. Lotter H., Wagner H., Saleh A. A., Cordell G. A., Farnsworth N. R.: Z. Naturforsch., C *34*, 677 (1979).

9. Rychlewska U.: J. Chem. Soc., Perkin Trans. 2, *1982*, 1641.
10. Rychlewska U.: Acta Crystallogr., C *39*, 1303 (1983).
11. Fronczek F. R., Malcolm A., Fisher N. H.: J. Nat. Prod. *46*, 170 (1983).
12. Duax W. L., Norton D. A.: *Atlas of Steroid Structures*, Vol. 1. New York, Plenum 1975.
13. Goodlett V. W.: Anal. Chem. *37*, 431 (1965).
14. Samek Z., Buděšínský M.: This Journal *44*, 558 (1979).
15. Samek Z.: This Journal *43*, 3210 (1978).
16. Le Cocq C., Lallemand J.-Y.: J. Chem. Soc., Chem. Commun. *1981*, 150.
17. Droździ B.: Dissert. Pharm. Pharmacol. *19*, 223 (1967).
18. Corfield P. W. R., Doedens R. J., Ibers J. A.: Inorg. Chem. *6*, 197 (1967).
19. Germain G., Main P., Woolfson M. M.: Acta Crystallogr., A *27*, 368 (1971).

Translated by Ž. Procházka.