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# THE STRUCTURE OF PHYSALINS F AND J FROM *PHYSALIS ANGULATA* AND *P. LANCIFOLIA**

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**Key Word Index**—*Physalis angulata*; *Physalis lancifolia*; Solanaceae; physalins B, F and J; structural elucidation.

**Abstract**—Physalins F and J are shown to be Physalin B 5β,6β-epoxide and 5α,6α-epoxide, respectively. The transformation of physalin F into physalin D (5,6-dihydro-5α,6β-dihydroxyphysalin B) and an acid-catalysed skeletal rearrangement of physalin F into isophysalin F are described.

## INTRODUCTION

In the preceding paper [1], it has been reported that physalins B, E, F, H and I occur together in the stems of *Physalis angulata* raised from seeds procured from Copenhagen, and that the Lucknow variety as well as *P. lancifolia* contain the physalins B, E and F in approximately equal proportion in addition to a new physalin G. By more careful separation of the components of both *Physalis* species, it was found that they contain a minor component which was named physalin J. Since the compositions of all the varieties are very similar, there is a remote likelihood of the Lucknow variety being synonymous, with *P. lancifolia*.

The structures of physalin E and H were discussed previously [1]. Evidence is now furnished to prove that the physalins F and J are respectively 5β,6β-(2) and 5α,6α-epoxides (3) of physalin B (1), and their chemical reactions are described.

## RESULTS AND DISCUSSION

Physalins F (2) and J (3) were isometric epoxides with a molecular formula $C_{28}H_{30}O_{10}$ and are closely related to physalin B (1) ($C_{28}H_{30}O_9$). All the functional groups of 1 [2], including the methylene oxide bridge between C-14 and C-26 (C-26 *H*a, δ 4.27 *dd*, $J$ = 14 Hz; C-26 *H*b, δ 3.57 *d*, $J$ = 14 Hz) and tertiary hydroxyl at C-13 (δ 6.35 *s*), could be readily identified in their NMR spectra (Table 1). However, physalins F and J differ from physalin B in the 6-H resonances; it was observed as an olefinic proton at δ 5.62 *m* in physalin B [2] but in physalin F it was detected at δ 3.26 *m*, and in physalin J at δ 3.03 *m*, suggesting that C-6 has an oxygen function in both these compounds. Since this oxygen is not present as an additional hydroxyl, it could be present as an epoxide between C-5 and C-6 or as an ether at C-6 only. The latter functionality was not supported by their molecular formula or NMR spectra.

Recently Glotter *et al.* [3] reported the isolation of physalin B 5β,6β-epoxide (2) from *Physalis minima* and recorded that it was identical with one of two epoxides synthesized from physalin B by the epoxidation with *m*-chloroperbenzoic acid. Their constants (6H, δ 3.23, *d*, $J$ = 2.5 Hz, mp 243–245° and $[\alpha]_D$ −67.2°) differed prominently from those of physalin F, while those of physalin B 5α,6α-epoxide closely agreed with those of physalin J (Table 1). This prompted us to prepare the physalin B epoxides by the action of *m*-chloroperbenzoic acid (or perphthalic acid) in chloroform solution followed by careful separation of the mixture on a Si gel column. Although the reaction mixture showed only two spots on TLC ($R_f$ = 0.77 and 0.74), three products were separated from the reaction mixture by chromatography on Si gel, the third one having an $R_f$ value of 0.45. The first two products were found identical with physalin F and physalin J, respectively, (mmp and IR) and also with the samples of physalin B 5β,6β- and 5α,6α-epoxides, respectively, (IR) which were synthesized by Glotter *et al.* [3]. Also, the Cotton effect and CD values agreed closely. On the basis of the Cotton effect and CD values, physalin F is considered to be physalin B 5β,6β-epoxide (2) and physalin J is the corresponding 5α,6α-epoxide (3).

The formation of the third compound (4) obviously took place from one of the two epoxides during the chromatographic separation, probably by the hydrolytic opening of the epoxide ring. This was confirmed by running the two epoxides separately on different Si gel columns; the 5β,6β-epoxide (2) was extensively destroyed and gave rise to the third compound ($R_f$ = 0.45). The isomeric 5α,6α-epoxide (3) was recovered almost completely.

During the study of physalins F and J, it was noticed that physalin F undergoes a rearrangement under the influence of sulfuric acid in acetic acid. The new compound, isophysalin F (5), crystallized from ethyl acetate–benzene, as colourless needles, $C_{28}H_{30}O_{10}$, mp 249–251°, $\lambda_{max}^{EtOH}$ 250 nm. Under similar conditions, physalin J

* Part 2 in the series 'Physalins E and H, New Physalins from *Physalis angulata* and *P. Pancifolia*'. For part 1 see the preceding paper.

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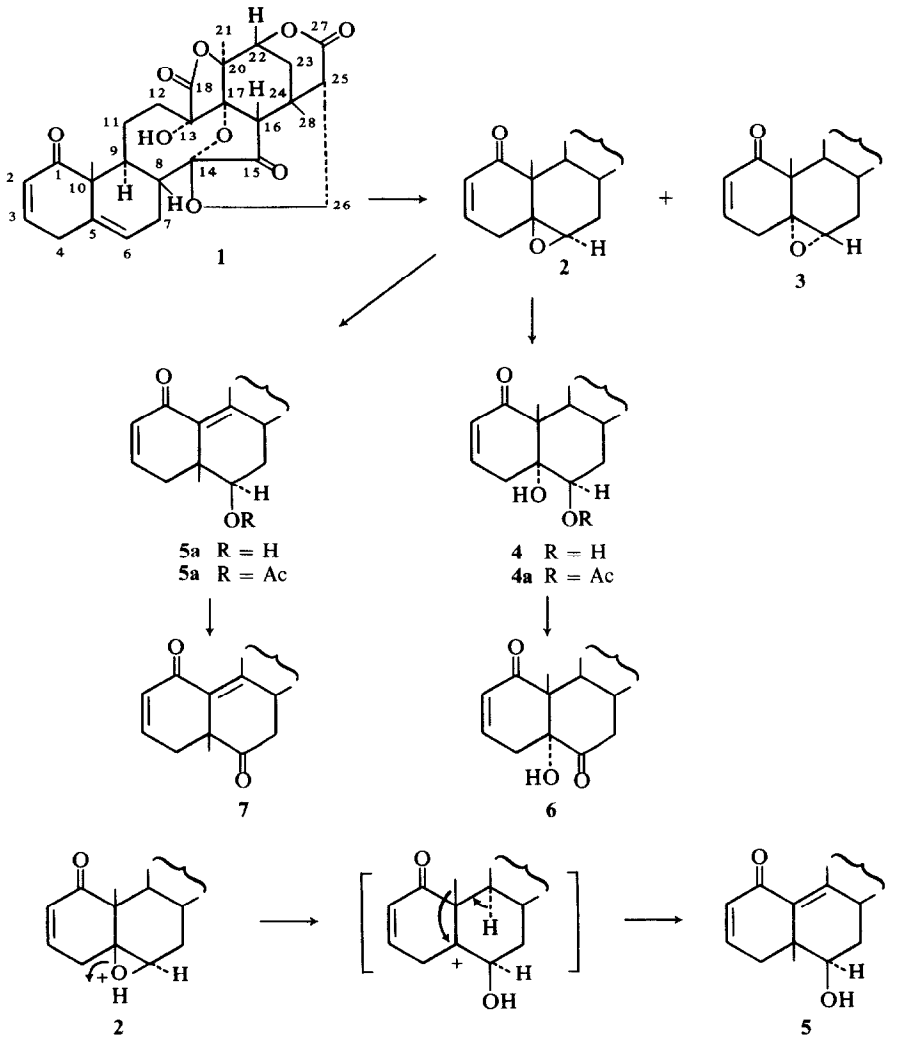

Table 1. NMR chemical shifts of relevant protons in new physalins and their derivatives*

| Compound | 2–H | 3-H | 6-H | 7-H | 22-H | 26-$H_a$ | 26-$H_b$ | 13-OH | Other groups |
|---|---|---|---|---|---|---|---|---|---|
| **1**† | 5.8 *d* (10) | 6.88 *dt* (10, 3) | 5.62 *m* | — | 4.57 *m* | 4.28 *dd* (13, 4) | 3.60 *d* (13) | 6.26 *s* | — |
| **2** | 6.01 *dd* (10, 4) | 6.93 *dm* (10) | 3.26 *m* | — | 4.56 *m* | 4.27 *dd* (14, 4) | 3.57 *d* (14) | 6.35 *s* | — |
| **3** | 5.72 *dd* (10, 4) | 6.61 *dm* (10) | 3.03 *m* | — | 4.59 *m* | 4.28 *dd* (14, 4) | 3.60 *d* (14) | 6.31 *s* | — |
| **4** | 5.73 *d* (10) | 6.61 *dm* (10) | — | — | 4.55 *m* | 4.20 *m* | 3.60 *d* (14) | 5.68 *s* | 5-OH 4.19 *s* 6-OH 4.85 *d* (4) |
| **5** | 5.84 *dd* (10, 3) | 6.76 *dd* (12, 4) | 3.87 *m* | — | 4.56 *m* | 4.27 *dd* (14, 4) | 3.58 *dd* (14) | 5.95 *s* | 5-OH 5.62 *d* (5) |
| **5a** | 5.87 *dd* (12, 2) | 6.76 *dm* (12) | 5.10 *t* (2) | — | 4.56 *m* | 4.27 *dd* (13, 4) | 3.37 *d* (13) | 6.06 *s* | — |
| **7** | 5.96 *dd* (11, 2) | 6.87 *dd* (10, 4) | — | 3.90 *dd* (12, 8) 3.16 *d* (12) | 4.64 *m* | 4.35 *dd* (14, 4) | 3.65 *d* (13) | 6.34 *s* | 8-H 3.19 *d* (7) |

*Spectra were taken in DMSO-$d_6$ solution; chemical shifts are $\delta$ values; coupling constants ($J$ in parentheses) are given by Hz.
† Ref. [2].

(3) did not give rise to isophysalin F, but gave a low yield of a compound, which was identical (TLC) with the third compound (4) secured during the Si gel chromatographic separation of the physalin B epoxides. Physalin F (2) thus gave rise to two different products, isophysalin F (5) and the Si gel-catalysed reaction product (4). The latter crystallized as colourless shining plates $C_{28}H_{32}O_{11}$, mp 286–287°. It gave a monoacetate (4a) and on Jones' oxidation a hydroxy-ketone (6), suggesting that 4 could be a diol whose NMR spectrum showed one secondary hydroxyl at $\delta$ 4.85 (*d*, $J$ = 4 Hz) and a tertiary hydroxyl at $\delta$ 4.19(*s*). The diol 4 was found to be identical (mmp, IR, and NMR) with physalin D isolated earlier by Mulchandani [4] from *Physalis minima*, who assigned it as 5,6-dihydro-5$\alpha$-6$\beta$-dihydroxyphsalin B (4). The $\alpha$-configuration of the C-5 hydroxyl in 4 was confirmed by measuring ORD and CD spectra, which showed the strong negative Cotton effect of the enone $n \rightarrow \pi^*$ band near 340 nm and the two negative CD bands of the $n \rightarrow \pi^*$ bands of the C-1 and C-15 carbonyls near 340 nm [1, 3, 5].

Isophysalin F (5) gives rise to an acetate (5a) by acetylation and a ketone (7) with Jones' reagent, indicating the presence of a secondary hydroxyl. Unlike physalin F (2), isophysalin F (5) showed a bathochromic shift to 250 nm ($\varepsilon$ 8200) indicating a probable extension of the enone chromophore of the ring A. Its NMR spectrum provided valuable information to assign structure (5). It contained the usual enonic protons at $\delta$ 5.84 (2H, *dd*, $J$ = 10, 3 Hz) and $\delta$ 6.76 (3H, *dd*, $J$ = 12, 4 Hz) and no other olefinic protons could be observed. The C-6 proton in (5) appeared at $\delta$ 3.87 (*m*), whereas in its acetate (5a) it was noticed at $\delta$ 5.10 (*t*, $J$ = 2 Hz). This suggests that the C-6 proton could be equatorial, because it bisects the two C-H bonds at position 7. Furthermore, there is an ill-defined signal at $\delta$ 3.06 (*m*) for 5, which integrates for a single proton and the same proton appears at $\delta$ 3.14 for its acetate. These two signals can be assigned to an allylic proton to a newly formed, tetrasubstituted double bond which was responsible to a bathochromic shift in the UV spectrum of 5. The isophysalin F can, therefore, be formulated as 5, in which the original C-10 methyl has shifted to C-5 and a tetrasubstituted double bond has formed between C-9 and C-10. Since the epoxide ring was already shown to be 5$\beta$,6$\beta$-oriented in 2, the methyl group is presumed to have migrated over the $\beta$-face.

The NMR spectrum of the ketone (7) obtained from isophysalin F (5) confirms the position of the tetrasubstituted double bond between C-9 and C-10. There were two groups of proton signals. Firstly a multiplet, which was regarded as a *dd* was at $\delta$ 3.80, 3.88 and $\delta$ 3.92, 4.00, all integrating for one proton. Secondly, a pair of doublets at $\delta$ 3.10, 3.22 and $\delta$ 3.15, 3.22 each integrating for one proton. These chemical shifts and coupling constants suggest that they should be assigned to the C-7 and C-8 protons. Since the $\delta$ 3.06 (*m*) signal of the allylic C-8 proton of (5) is not likely to be disturbed due to oxidation of the C-6 hydroxyl, the additional proton in this region must belong to the C-7 methylene group. Clearly the doublet signal at $\delta$ 3.15, 3.22 can be assigned to the allylic C-8 proton and the signal at $\delta$ 3.10, 3.22 can be assigned to C-7-$\underline{H}_a$. The remaining *dd* signal is assigned to the axial C-7-$\underline{H}_b$. This low field signal for the methylene protons $\alpha$ to a carbonyl is not unknown [5].

The rearrangement of 5$\beta$,6$\beta$-epoxide physalin F (2) into isophysalin F (5) in the presence of an acid can be visualized as indicated above. The cause of this rearrangement appears to be due to a steric repulsion between the 5$\beta$,6$\beta$-epoxide and the C-10$\beta$ methyl. The proton attack at the epoxide oxygen may give a carbocation which causes the migration of the C-10 methyl to C-5 over the $\beta$-face and gives a tetrasubstituted double bond between C-9 and C-10, although the exact mechanism of this rearrangement is not clear. Similar methyl rearrangements have been noticed earlier [6–9].

## EXPERIMENTAL

The seeds of *Physalis angulata* (Solanaceae) were secured from Copenhagen (Denmark) and the plants grown in the Botanic Farm, Andhra University, Waltair, India.

*Extraction of the stems of* Physalis angulata. The dry stems were collected and extracted successively with *n*-hexane and $CHCl_3$ as described previously [1]. The latter extract was fractionated over a column of Si gel using several eluents and the various compounds isolated are indicated in Table 2.

The whole plant, *P. lancifolia*, was similarly extracted and all the above physalins were isolated and identified.

*Physalin B* (1). Crystallized from MeOH as colourless needles, mp 268–270°, identified by comparison with an authentic sample (mmp and IR) [2].

*Physalin F* (2). Crystallized from MeOH–$Me_2CO$ (1:1) as colourless stout needles, mp 295–296°; $[\alpha]_D$ −20° (*c*, 0.5, $Me_2CO$); $R_f$ 0.77 (Si gel, EtOAc–$C_6H_6$, 7:3); positive Cotton effect; CD 338 nm ($\Delta\varepsilon$ +1.95) 352.5 nm ($\Delta\varepsilon$ +1.68). (Found: C, 63.25; H, 5.90; $M^+$ 526. $C_{28}H_{30}O_{10}$ requires: C, 63.87; H, 5.74%). $\lambda_{max}^{EtOH}$ 218 nm ($\varepsilon$ 10000); $\nu_{max}^{Nujol}$ $cm^{-1}$; 3400 (OH), 1800, 1758, 1740, 1670, 1130, 1080, 1060.

*Physalin J* (3). Crystallized from $CHCl_3$–MeOH (1:1) as colourless shining plates, mp 268–270°; $[\alpha]_D$ −60° (*c*, 0.5, $Me_2CO$); $R_f$ 0.74 (Si gel, EtOAc–$C_6H_6$, 7:3); negative Cotton effect; CD 336 nm ($\Delta\varepsilon$ −1.86) 340 nm ($\Delta\varepsilon$ −1.79). (Found: C, 63.12; H, 5.6. $C_{28}H_{30}O_{10}$) requires: C, 63.87; H, 5.74%). $\lambda_{max}^{EtOH}$ 220 nm ($\varepsilon$ 9200); $\nu_{max}^{Nujol}$ $cm^{-1}$: 3400 (OH), 1792, 1757, 1738, 1665, 1120, 1085, 1072.

*Physalin G.* Crystallized from MeOH into thin colourless needles, mp 295–96°; $[\alpha]_D$ +17° (*c*, 0.5, $Me_2CO$); $R_f$ 0.65 (EtOAc–$C_6H_6$, 7:3). (Found: C, 63.52; H, 5.89; $M^+$ 526. $C_{28}H_{30}O_{10}$ requires: C, 63.87; H, 5.74%); $\lambda_{max}^{EtOH}$ 218 nm ($\varepsilon$ 10800); $\nu_{max}^{KBr}$ $cm^{-1}$: 3400, 1790, 1765, 1740, 1665.

*Epoxidation of physalin B to yield physalin B 5$\beta$,6$\beta$-epoxide* (2) *and physalin B 5$\alpha$,6$\alpha$-epoxide* (3) *and the 5,6-dihydro-5$\alpha$,6$\beta$-dihydroxyphysalin B* (4). Physalin B (500 mg) in $CHCl_3$ (500 ml) was treated with a soln of *m*-chloroperbezoic acid (250 mg) in $C_6H_6$ (30 ml) [or monoperphthalic acid in $Et_2O$ (25 ml) for 12 hr]. The mixture was kept for about 24 hr at room temp. and

Table 2. Isolation of new physalins from *P. angulata*

| Fractions 500 ml | Eluent | Compounds | Yield (g) |
|---|---|---|---|
| 1–8 | $C_6H_6$ | Oil | 0.30 |
| 9–11 | $C_6H_6$–EtOAc (85:15) | Physalin B | 0.65 |
| 12–13 | $C_6H_6$–EtOAc (85:15) | Physalin B and F | 0.52 |
| 14–28 | $C_6H_6$–EtOAc (85:15) | Physalin F | 1.40 |
| 29–46 | $C_6H_6$–EtOAc (85:15) | Physalin J | 0.20 |
| 47–56 | $C_6H_6$–EtOAc (75:25) | Oil | 0.70 |
| 51–71 | $C_6H_6$–EtOAc (70:30) | Physalin G | 1.00 |
| 72–86 | $C_6H_6$–EtOAc (65:35) | Physalin E | 1.10 |

diluted with $CHCl_3$ (50 ml). The total soln was washed with 2% aq. $NaHCO_3$ soln, 1 N HCl and $H_2O$ successively. The organic layer was dried over dry $Mg_2SO_4$ and evapd. The residue showed two spots on Si gel TLC (EtOAc–$C_6H_6$, 6:4) and could not be fractionally crystallized from a number of solvents. Hence it was adsorbed on Si gel-G (100–200 mesh, 3 g) and placed on to a Si gel (15 g), column (45 cm × 2.6 cm). Using EtOAc–$C_6H_6$ mixtures as eluent, several fractions (100 ml each) were collected to give compounds **2**, **3** and **4**.

*Physalin B 5β,6β-epoxide* (**2**) (*physalin F*). Eluated with $C_6H_6$–EtOAc (88:12) (110 mg) and crystallized from $Me_2CO$–MeOH (1:1) as colourless stout needles, mp 293–95°; $R_f$ 0.77 (EtOAc–$C_6H_6$, 7:3), identical with physalin F (mmp and IR) and also with a sample of **2**, mp 262–264°, (IR) kindly provided by Kirson [3].

*Physalin B 5α,6α-epoxide* (*physalin J*) (**3**). Eluated with $C_6H_6$–EtOAc (88:12) (120 mg) and crystallized from $Me_2CO$ as small colourless shining plates, mp 267–69°; $R_f$ 0.74 (EtOAc–$C_6H_6$, 7:3), identical with physalin J (mixed mp and IR) and also with a sample of **3**, mp 243–245°, kindly provided by Kirson [3].

*5α,6β-dihydroxy-5,6-dihydrophysalin-B* (*physalin D*) (**4**). Eluated with $C_6H_6$–EtOAc (75:25) (140 mg) and crystallized from MeOH as white shining plates, mp 286–287°; $R_f$ 0.45 (EtOAc–$C_6H_6$, 7:3), identical with an authentic sample of physalin D (mmp and IR) kindly provided by Mulchandani [5]. (Found: C, 61.10; H, 6.12. $C_{28}H_{32}O_{11}$ requires: C, 61.82; H, 5.92%); $\lambda_{max}^{EtOH}$ 227 nm (ε 6500); $\nu_{max}^{KBr}$ $cm^{-1}$: 3400 (OH), 1792 (γ-lactone), 1757 (five membered ring ketone), 1742, 1665; ORD (dioxan), $[M]_{355\,nm}$ −3500° (min), $[M]_{315}$ +3300 (max), $[M]_{240}$ −6500° (min), $[M]_{218}$ +24300° (max); CD (dioxan) $\lambda_{max}$ 344 nm (Δε −2.28), 339 (−2.26), 333 (−2.35), 266 (−0.03), 222 (−6.11) (strongly positive at shorter wavelengths). The acetate (**4a**) ($Ac_2O$–Py, 100°, 1 hr) was obtained as colourless needles from MeOH, mp 241–242°.

*Oxidation of 5,6-dihydro-5α,6β-dihydroxyphysalin B to 5,6-dihydro-5α-hydroxyphysalin 5-B-one* (**6**). Compound (**4**) (50 mg) in aldehyde free $Me_2CO$ (35 ml) was treated with Jones' reagent (6 drops) for 20 min. After the usual work-up the residue was crystallized from MeOH as small colourless needles (30 mg), mp 294–295°.

*Hydrolysis of physalin F* (**2**) *on a Si gel column to yield 5,6-dihydro-5α,6β-dihydroxyphysalin B* (*physalin D*) (**4**) Physalin F (25 mg) was adsorbed on Si gel G (100–200 mesh, 1.5 g) and the column (45 × 2.6 cm) was wet with $C_6H_6$. The column was eluted with $C_6H_6$–EtOAc (75:25) mixture. Several fractions (100 ml each) were collected. The residue (20 mg) from the fractions which showed a single spot on TLC was crystallized from MeOH, mp 286–287°, and was identical with **4** from the epoxidation of Physalin B.

Physalin J (25 mg) was similarly chromatographed on a Si gel-G column. Elution with $C_6H_6$–EtOAc (75:25) (100 ml) gave the starting compound (20 mg).

*Acid-catalysed rearrangement of physalin F* (**2**) *to isophysalin F* (**5**). Physalin F (150 mg) dissolved in glacial HOAc (10 ml) was heated with 1 N $H_2SO_4$ (10 drops) on a steam bath. After 1 hr, the mixture was poured into $H_2O$ (100 ml) and the product was extracted with $CHCl_3$ (50 ml × 3). The combined $CHCl_3$ extracts were washed with 2% aq $NaHCO_3$ soln, 1 N HCl, and $H_2O$, successively, dried over dry $Mg_2SO_4$, and evapd. Isophysalin F (**5**) crystallized from MeOH as shining needles, mp 249–251° (120 mg); (Found: C, 63.40; H, 5.81. $C_{28}H_{30}O_{10}$ requires: C, 63.87; H, 5.74%), $\lambda_{max}^{EtOH}$ 250 nm (ε 8200); $\nu_{max}^{KBr}$ $cm^{-1}$: 3400 (OH), 1792 (γ-lactone), 1758 (five membered ring ketone), 1732 (δ-lactone), 1670 (α:β-unsaturated 6 membered ring ketone).

*The acetate* (**5a**). Treatment of **5** with Py–$Ac_2O$ on a steam bath for 1 hr gave (**5a**) which crystallized from MeOH as colourless needles, mp 268–269°; (Found: C, 63.10; H, 5.75. $C_{30}H_{32}O_{11}$ requires: C, 63.42; H, 5.68%); $\lambda_{max}^{EtOH}$ 252 nm (ε 4400); $\nu_{max}^{KBr}$ $cm^{-1}$: 3400, 1795, 1757, 1735, 1715 and 1670.

*Oxidation of isophysalin F* (**5**) *to dehydroisophysalin F* (**7**) Isophysalin F (50 mg) in aldehyde free $Me_2CO$ (35 ml) was treated with Jones' reagent (6 drops) for 15 min. After usual work-up, the residue was crystallized from MeOH as small colourless needles (42 mg); mp 286–287°, (Found: C, 63.90; H, 5.50. $C_{28}H_{28}O_{10}$ requires: C, 64.12; H, 5.38%), $\lambda_{max}^{EtOH}$ 248 nm (ε 4000), $\nu_{max}^{EtOH}$ $cm^{-1}$: 3400, 1795, 1758, 1735, 1700 and 1665.

*Acid hydrolysis of physalin J* (**3**) *to 5,6-dihydro-5α,6β-dihydroxyphysalin B* (*physalin D*) (**4**). Physalin J (50 mg) in glacial HOAc (5 ml) was heated with 1 N $H_2SO_4$ (3 drops) on a steam bath for 2 hr. After work up, the product crystallized from MeOH as white shining plates, mp 286–287° (20 mg); $R_f$ 0.45 (EtOAc–$C_6H_6$, 7:3); identical with the diol **4** obtained above.

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