TABLE 1

Sl. no	R_f	%	Name
1.	1.00	3.74	Cholesterol (Cholest-5-en-3β-ol)
2.	1.26	5.71	Campesterol (24-Methylcholesta-5-en-3β-ol)
3.	1.34	19.4	Stigmasterol (24-Ethylcholesta-5,22-dien-3β-ol)
4.	1.50	28.02	β-Sitosterol (24-Ethylcholesta-5-en-3β-ol)
5.	1.75	23.85	∝-Spinasterol (24-Ethylcholesta-7,22-dien-3β-ol)
6.	1.75	11.37	22-Dihydrospinasterol (24-Ethylcholesta-7-en-3β-ol)

sence of both Δ^5- and Δ^7-sterols is quite unique. The most interesting aspect is the presence of significant amount of cholesterol (3.74%) which is rare in plant kingdom and so far reported in traces, except in *Lantana indica* where it occurs in considerable amount (7%)[5].

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References

1. "The Wealth of India-Raw Material", C.S.I.R., New Delhi, 1952, Vol. III, p. 185.
2. Y. KIMURA, M. MORI and A. SUZUKI, *Agric. Biol. Chem.*, 1981, 45, 4915.
3. D. K. MATHELA, A. K. PANT and C. S. MATHELA, *Phytochemistry*, 1984, 23, 2029.
4. D. K. MATHELA, C. S. MATHELA and J. TASHKINEN, *J. Indian Chem. Soc.*, 1986, 63, 603.
5. M. M. GOYAL and K. KUMAR, *Indian Drugs*, 1984, 22, 41.

Chemical Constituents of *Physalis minima* var. *indica*[1]

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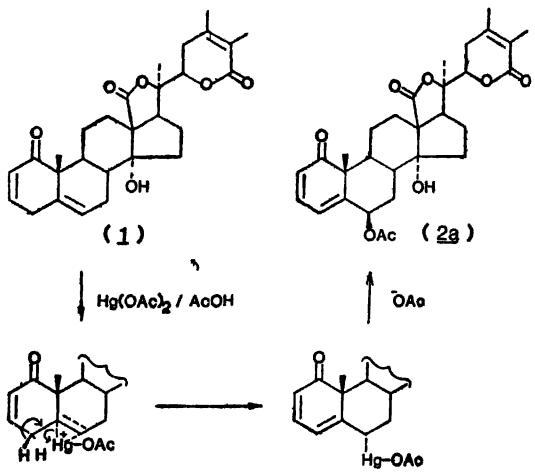
IN continuation of our work on the withasteroids of *Physalis peruviana*[2], we took up chemical investigation of *Physalis minima* var. *indica*, an annual herb of medicinal value which is distributed throughout the warmer parts of India[3,4]. A systematic chemical investigation of this plant yielded seven withasteroids and two flavone glucosides in addition to β-sitosterol, its glucoside and the previously reported[5] withaphysalin A (1). Four of these were new and the structures of these new steroids, viz. physalindicanols A and B withaminimin and withaphysalin E (2) were reported elsewhere[6-8]. The remaining compounds were identified as physalin B[9], physalin D[10], withaphysalin C[11] and 3-*O*-glucosides of kaempferol and quercetin[12], the occurrence of which in this plant is being reported here for the first time. The ^{13}C nmr data of physalins B and D that have not yet been recorded in the literature are also reported here with assignment of resonance signals to different carbon atoms of these two molecules, the assignment being based on reported spectral data[13] of related molecules and supported by their SFORD spectra.



In this communication, an unambiguous chemical proof in support of the structure of withaphysalin E (2) is provided by a one-step chemical transformation of withaphysalin A (1) to withaphysalin E acetate (2a). When a solution of withaphysalin A in glacial acetic acid was warmed at 80° for 3 h with mercuric acetate, the reaction mixture, on usual work-up, yielded withaphysalin E acetate as the sole product The mercuric acetate induced acetoxylation of steroidal 2,5-dien-1-ones has been studied[14] by us and the product has been found to be 6β-acetoxy-2,4-dien-1-one in each case. The β-orientation of the 6-acetoxy function in 2a was ascertained from the chemical shift of 19-methyl which is known to be around δ 1.24 in 6∝-isomers and around δ 1.42 in its 6β-counterparts[15]. The exclusive formation of 6β-acetoxy derivative deserves comments and it is conjectured that the first step is the formation of a cyclic mercuronium ion[16] by addition of ^+HgOAc on 5,6-double bond from the ∝-side of the molecule ; the exclusive formation

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of 5α,6α-epoxide of withaphysalin A[5] by treatment with *m*-chloroperbenzoic acid lends credence to α-attack. The opening of the cyclic complex leads to Δ^4-6-mercurated compound which then undergoes S_Ni type substitution to give **2a** (Fig. 1).

Experimental

The dried and pulverised whole plant of *Physalis minima* var. *indica* (4.3 kg) were extracted with petroleum ether (b.p. 60 – 80°) and then with 95% ethanol. Chromatography of the concentrated petroleum ether extract (70 g) over silica gel and elution with solvents of increasing polarity yielded β-sitosterol (0.43 g) from C_6H_6 eluates, physalin B (2.5 g) from the early fractions of C_6H_6 – EtOAc (4 : 1) eluates, physalindicanol A (86 mg) and physalindicanol B (65 mg) from the later fractions of C_6H_6 EtOAc (4 : 1) eluates, and withaphysalin A from C_6H_6 – EtOAc (3 : 1) eluates. The major compound, physalin B showed m.p. 268° (lit[9]. 271°); ^{13}C nmr ($CDCl_3$) δ_c 208.5 (s, C-15), 205.1 (s, C-1), 172.7 (s, C-18), 167.1 (s, C-26), 146.6 (d, C-3), 134.3 (s, C-5), 127.5 (d, C-2), 124.8 (d, C-6), 107.7 (s, C-14), 81.3 (s, C-20), 80.6 (s, C-17), 79.8 (s, C-13), 77.3, (d, C-22), 60.9 (t, C-27), 56.3 (d, C-16), 52.9 (d, C-8), 51.1 (s, C-10), 40.4 (d, C-25), 33.5 (t, C-4), 33.2 (d, C-9), 32.9 (t, C-12), 31.4 (s, C-24) 29.9 (t, C-23), 26.7 (t, C-7), 26.1 (t, C-11), 25.0 (q, C-21), 21.8 (q, C-19) and 18.1 (q, C-28).

The alcoholic extract of the plant material was concentrated under reduced pressure to a syrup, diluted with equal volume of water and extracted successively with $CHCl_3$ and EtOAc The chloroform-soluble fraction of the alcoholic extract on repeated chromatography over silica gel and elution with C_6H_6, C_6H_6 – EtOAc mixtures and EtOAc yielded an additional quantity of physalin B (0.34 g) and withaphysalin A (21 mg) besides withaphysalin C (42 mg), physalin D (5 16 g), withaphysalin E (65 mg), withaminimin (30 mg) and β-sitosterol glucoside (0.4 g). The major product, physalin D showed m.p. 262° (lit[10]. 262 – 63°); ^{13}C nmr ($CDCl_3$) δ_c 210.1 (s, C-15), 205.2 (s, C-1), 173.4 (s, C-18), 167.5 (s, C-26), 142.5 (d, C-3), 128.5 (d, C-2), 108.1 (s, C-14), 81.8 (s, C-20), 81.4 (s, C-17), 80.1 (s, C-13), 77.6 (s, C-5), 77.6 (d, C-22), 74.4 (d, C-6), 61.3 (t, C-27), 55.6 (d, C-16), 55.1 (s, C-10), 50.8 (d, C-8), 39.6 (d, C-25), 36.3 (t, C-4), 32.7 (t, C-12), 31.4 (d, C-9), 31.3 (s, C-24), 28.1 (t, C-23), 26.8 (t, C-7), 26 0 (t, C-11), 25.7 (q, C-21), 22.4 (q, C-19) and 14.1 (q, C-28).

Ethyl acetate-soluble fraction of the alcoholic extract on repeated chromatography over silica gel afforded kaempferol-3-*O*-glucoside (62 mg) and quercetin-3-*O*-glucoside (85 mg) from C_6H_6 – EtOAc (1 : 1→2 : 3) eluates.

Conversion of withaphysalin A (**1**) *to withaphysalin E monoacetate* (**2a**): To a solution of withaphysalin A (20 mg) in glacial acetic acid (10 ml) was added mercuric acetate (35 mg) and the mixture warmed at 80° for 3 h and then cooled when shining crystals of mercurous acetate separated out. The reaction mixture was freed from inorganic salts by filtration and organic solvents by evaporation under reduced pressure to yield a residue which was chromatographed over a small bed of silica gel. Elution of the column with petroleum ether – EtOAc (3 : 2) yielded a microcrystalline white powder, m.p. 257 – 59°, identical in all respects (co-tlc, nmr, uv) with withaphysalin E acetate, prepared from withaphysalin E[8] by treatment with Ac_2O and pyridine.

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References

1. Part 18 of withasteroids, Part 17 communicated to *Phytochemistry*, for Part 16 see *Tetrahedron Lett.*, 1987, 28, 2025.
2. P. Neogi, M. Sahai and A. B. Ray, *Phytochemistry*, 1987, 26, 243.
3. "The Wealth of India. A Dictionary of Indian Raw Materials & Industrial Products", C.S.I.R. Publication, New Delhi, 1969, Vol. 8, p. 38.
4. K. R. Kirtikar and B D. Basu, "Indian Medicinal Plants", Singh & Singh Publication, Dehradun, 1975, Vol. 3, p. 1768.
5. M. Sahai and I. Kirson, *J. Nat Prod*, 1984, 47, 527.
6. S. C. Sinha, A. Ali, A. Bagchi, M. Sahai and A. B. Ray, *Plant Medica*, 1987, 55.
7. H. E. Gottlieb M. Cojocaru, S. C. Sinha, M. Sahai, A. Bagchi, A. Ali and A. B. Ray, *Phytochemistry*, 1987, 26, 1801.
8. S. C. Sinha, A. B. Ray, Y. Oshima, A. Bagchi and H. Hikino, *Phytochemistry*, 1987, 26, 2115.
9. T Matsuura, M. Kawai, R. Nakashima and Y. Butsugan, *J. Chem Soc. (C)*, 1970, 664.
10. N. B. Mulchandani, S. S. Iyer and L. R. Badheka, *Planta Medica*, 1979, 37, 268.
11. I. Kirson, Z. Zaretskii and E. Glotter, *J. Chem. Soc., Perkin Trans. 1*, 1976, 1244.
12. J. Heilbron, A. H. Cook, H M. Bumbury and D. H. Hey, "Dictionary of Organic Compounds", Eyre & Spottiswoode, London, 1965, Vol. 1, p. 290; Vol. 3, p. 1966.
13. M. Kawai, T. Matsuura, S. Kyuno, H. Matsuki, M. Takenaka, T. Katsuoka, Y. Butsugan and K. Saito, *Phytochemistry*, 1987, 26, 3313.
14. S. C. Sinha, S. Kundu, R. Maurya and A. B Ray, "Proceedings of 16th IUPAC Symposium", Kyoto, 1988, p 180.
15. M. Ishiguro, A. Kajikawa, T. Haruyama, Y. Ogura, M. Okubayashi, M. Morisake and N. Ikekawa, *J. Chem. Soc., Perkin Trans. 1*, 1975, 2295.
16. I. Alkyoni, *Chem. Ber.*, 1962, 95, 279; D J. Rawlinson and G Sosnovsky, *Synthesis*, 1973, 567.