Phytochemistry, 1974. Vol. 13, pp. 2239 to 2245. Pergamon Press. Printed in England.

TWO NEW STEROLS FROM *PHYSALIS FRANCHETII* FRUIT*

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(*Received* 12 *March* 1974)

Key Word Index—*Physalis franchetii*; Solanaceae; fruit phytosterols; physanols A and B.

Abstract—Two new steroids physanol A, 3β-benzoyloxy-6-oxo-stigmast-7,20-diene-11α-ol and physanol B, 3β-benzoyloxy-6-oxo-stigmast-7-ene-11α-ol have been isolated from the fruit of *Physalis franchetii*.

INTRODUCTION

Physalis franchetii Mast (*Physalis alkekengi* var. *franchettii Host*), is a lantern plant of Chinese origin that is now grown in Indian gardens.[1] Its fruit, sold under the name of Kaknaj, is used in the Unani system of medicine as a diuretic, stimulant[2] and anthelmintic.[3] Nishimoto[4] isolated an alkaloid, 3-(tigloyloxy)-tropane from *Physalis alkekengi*, Matsurra *et al.*[5–7] have isolated three novel steroids from *P. alkekengi var. franchetii* and Roynand *et al.*[8] have reported a flavonoid glycoside in the leaves of *P. alkekengi*. This paper is concerned with the structures of two unusual steroids encountered in the fruit of *P. franchetii*.

Hexane extracts of the powdered seeds from unripe fruit on concentration yielded a crystalline mass. TLC showed this material to be a mixture of three compounds A, B and C. The crude crystalline mixture was chromatographed on neutral alumina. Elution with hexane:benzene afforded compound A while the benzene eluate gave compound B. Compound C, eluted with benzene:chloroform, was identified as β-sitosterol. Compounds A and B have not been previously recorded and were designated as physanol A and physanol B, respectively.

RESULTS AND DISCUSSION

Physanol A analysed for $C_{36}H_{50}O_4$(M^+ 546) and gave a positive Liebermann–Burchard test. Its IR and PMR spectra also indicated it to be a steroid. The IR spectrum displayed absorption at 3560 cm^{-1} (OH), 3075, 3030, 1604, 1585, 1425 cm^{-1} (aromatic), 2958, 2865, 1462, 1388 cm^{-1} (aromatic ester), 1680, 1627 cm^{-1} (enone), and 893 cm^{-1} (>C=CH_2

* Communication No. 1877 from the Central Drug Research Institute.

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[5] KAWAI, M., TAGA, T., OSAKI, K. and MATSUURA, T. (1969) *Tetrahedron Letters* 1087.
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group). Its UV maxima at 237 nm (ε, 21380) was later found to be the combined maxima of the benzyloxy and enone chromophores. The PMR spectrum exhibited signals for two quaternary methyls (3H each, at 0·65 and 0·93 ppm), two secondary methyls (3H each, at 1·07 and 1·00 ppm),* C<u>H</u>–O– (1H, at 3·78 ppm), –C<u>H</u>–O–CO– (1H, at 4·66 ppm), >C=C<u>H</u>$_2$ (Two 1H, at 4·86 and 4·95 ppm) >C=C<u>H</u>–CO– (1H, at 5·73 ppm) and C$_6$<u>H</u>$_5$– (2H, and 3H, at 7·53 ppm).

Physanol A readily formed a monoacetate, $C_{38}H_{52}O_5$ (M^+ 588) and its PMR spectrum displayed one acetyl singlet at 2·0 ppm. The secondary nature of this hydroxyl was indicated by a 1 ppm paramagnetic shift of the carbinol proton PMR signal on acetylation and by the formation of a mono oxo derivative, $C_{36}H_{48}O_4$ (M^+ 544) on Jones' oxidation of physanol A. Since the IR and PMR spectra of physanol A suggested the presence of a vinylidene group, it was treated with *m*-chloroperbenzoic acid. The IR spectrum of epoxy-physanol A, $C_{36}H_{50}O_5$ (M^+ 562) did not show ν_{max} 893 cm^{-1} but two new bands at 931 and 784 cm^{-1} assignable to C–O–C stretching of an epoxide and its PMR spectrum also lacked the vinylic singlets at 4·86 and 4·95 ppm. Instead, there was a narrow multiplet corresponding to two protons at 2·68 ppm assignable to the methylene protons on one of the carbons bearing the epoxide. These findings confirmed the presence of a vinylidene group in the molecule.

Hydrogenation of physanol A gave a dihydro product, $C_{36}H_{52}O_4$ (M^+ 548) while the dihydro as well as a tetrahydro derivatives were formed in a ratio of *ca* 8:1 when HOAc was the solvent. The IR and PMR spectra of dihydrophysanol A showed that only the vinylidene group had been reduced.

The PMR spectrum of tetrahydrophysanol A, $C_{36}H_{54}O_4$ (M^+ 550) did not show any olefinic proton signals. Its IR spectrum also showed a strong band at 1710 cm^{-1} for a ketone in a six-membered ring but none for the double bond. Tetrahydrophysanol A was, therefore, completely saturated and physanol A, therefore, contains only two double bonds.

The molecular formula of physanol A ($C_{36}H_{50}O_4$) and of its saponification products ($C_{29}H_{46}O_3$) in conjunction with its physicochemical data suggested that physanol A was a benzoate of a C_{29} steroid (stigmastane type). The stigmastane type of side chain in physanol A was revealed by a 3H triplet (*J* 7 Hz) at 1·1 ppm in its PMR spectrum (100 Hz). This signal could only be assigned to the Me protons of an ethyl group in the side chain. Further, in the MS of physanol A and its debenzoylated derivatives, there was a prominent loss of 139 a.m.u. corresponding to the elimination of the $C_{10}H_{19}$ side chain and in the MS of dihydrophysanol A ($C_{36}H_{52}O_4$), as well as tetrahydrophysanol A ($C_{36}H_{54}O_4$), there was a corresponding loss of 141 a.m.u. ($C_{10}H_{21}$) similar to that of β-sitosterol which also possesses a saturated C_{10} side chain. This data strongly suggests that the basic skeleton of physanol A was of the stigmastane type.

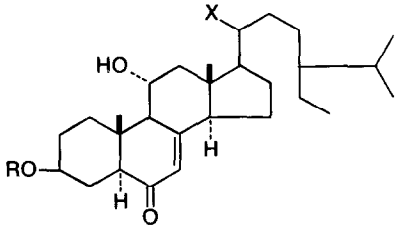
Physanol A was saponified and the products resolved into acidic and neutral fractions. The acidic fraction, was identified as benzoic acid by comparison with an authentic sample, m.m.p., superimposable IR spectra and TLC. The neutral fraction showed two spots on TLC and chromatography over neutral alumina afforded two crystalline substances, designated debenzoylphysanol A and debenzoylphysanol A_1 in order of increasing R_f

* Attention is drawn to the unusually deshielded location of the C-26, C-27 and C-29 methyl signals which appear because of the presence of the unusual C-20 double bond in physanol A. The spectrum of physanol B, in which this double bond is saturated, shows the usual chemical shifts of less than 0·9 ppm for the corresponding methyl signals.

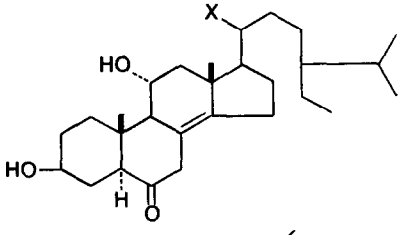
values. Debenzoylphysanol A $C_{29}H_{46}O_3$ (M^+ 442) showed an enone maximum at 245 nm (ε, 12250), which had been displaced by the absorption of the benzoyl group in the spectrum of physanol A. The presence of an enone was corroborated by IR absorption bands at 1670 and 1633 cm^{-1}. The IR spectrum also indicated the presence of OH (3533 cm^{-1}) and C=CH_2 (890 cm^{-1}) functions in the molecule. The PMR spectrum of this compound also exhibited a 1H quartet at 5·76 ppm and a pair of 1H broad singlets at 4·93 and 5·03 ppm assignable to C=CH–CO– and C=CH_2 groups respectively. A 1H doublet of multiplets and a very broad multiplet centred at 3·18 and 3·85 ppm were assignable to two methine protons adjacent to secondary hydroxyl groups, debenzoylphysanol A, therefore, contained all the functional groups present in physanol A except for the benzoate group which had been hydrolysed.

Debenzoylphysanol A_1 $C_{29}H_{46}O_3$ (M^+ 442) showed only end absorption around 208 nm (ε, 8142) and no enone absorption. Its IR spectrum also lacked the enone absorption bands but there was a band at 1708 cm^{-1}, which could be assigned to a six membered ring ketone. Its PMR spectrum showed no signal for C=C–CH_2–CO– but had a 2 H multiplet centred at 3·0 ppm assignable to the two protons of a methylene adjacent to a double bond and a carbonyl group (–C=C–CH_2–CO). Thus in the alkaline hydrolysis of physanol A, the carbonyl conjugated double bond had migrated out of conjugation to take up a tetrasubstituted position.

In a steroid molecule a vinylidene group can only be accommodated in the side chain. This inference also followed from the MS of physanol A, which showed facile cleavage of an unsaturated side chain ($C_{10}H_{19}$) from the M^+-C_6H_5COOH fragments. In the MS of steroids having double bonds at Δ^{22}, Δ^{24} or Δ^{25}, the side chain is eliminated along with two hydrogen atoms of the skeleton. In the case of physanol A, the elimination of its side chain was not accompanied by the loss of skeletal hydrogen atoms, since in the case of the dihydro-product the loss of the side chain fragment involved only two additional a.m.u. The vinylidene double bond could thus be located at Δ^{20}, Δ^{25} or Δ^{28} but since the PMR spectrum of physanol A did not show characteristic signals for –C–Me=CH_2 and –CH=CH_2 groups, the vinylidene group can only be at Δ^{20} position. The structure (**1**) accounts for the pair of singlets at 4·86 and 4·95 ppm, broadened by the allylic coupling with protons located at C_{22} and C_{17} in the PMR spectrum of physanol A.



(1) R = C_6H_5CO; X = CH_2
(2) R = H; X = CH_2
(4) R = C_6H_5CO; X = CH_3–



(3) X = CH_2

Physanol A possesses an enone chromophore in a six-membered ring. It could, therefore, occupy any of the following positions in the steroid skeleton, Δ^4, 3-oxo; Δ^5, 5-oxo; Δ^7, 6-oxo or $\Delta^{9(11)}$, 12-oxo. The double bond of the enone system in physanol A should, however, be placed so as to be able to take up a tetrasubstituted position, as observed during the alkaline hydrolysis leading to the formation of debenzoylphysanol A_1. This requirement can only be met if the enone group is present either at the $\Delta^{9(11)}$, 12-oxo or the

Δ^7, 6-oxo positions. The PMR signal of the enone proton in physanol A appeared as a quartet (*J*1·5 *Hz*) due to its allylic coupling with protons on γ-carbon atoms.[10] The splitting pattern (quartet) of the vinylic proton clearly supported a Δ^7, 6-oxo enone as it had two allylic protons available at C_9 and C_{14} to couple with. In the case of a $\Delta^{9(11)}$, 12-oxo enone, the vinylic signal should have appeared as a narrow doublet (*J*1·5 Hz) due to its coupling with only one allylic proton available at C_9. Further confirmation of this position of the enone in physanol A was achieved by its reduction with $NaBH_4$ which yielded a dihydroxy product, $C_{36}H_{52}O_4$ (M^+ 548), showing no UV absorption. The IR spectrum of this compound showed the presence of a trisubstituted double bond (793 and 815 cm^{-1}) but no carbonyl absorption. The PMR spectrum, however, showed a vinylic proton signal (1H) as a broad doublet (*J*5·0 Hz) centred at 5·56 ppm and a 1H triplet (*J*5·0 Hz) centred at 4·26 ppm due to the carbinol proton of the newly generated hydroxyl group, which was coupling with the olefinic H and a C_5 proton and thus confirmed the Δ^7, 6-oxo assignment of the enone (**2**).

The oxidation product of physanol A displayed an IR absorption band at 1708 cm^{-1} characteristic of a six membered ring ketone so that the hydroxyl group must be present in a six-membered ring. Furthermore the PMR spectrum of ketophysanol A showed a 2H singlet at 3·11 ppm and another sharp singlet at 2·1 ppm, probably representing 1H, together with other signals. Obviously, these downfield signals were due to the protons on carbon atoms adjacent to the carbonyl group. The singlet nature of both these signals requires that these α-protons should have no vicinal protons to coupled with. The only position for the keto group that satisfies this requisite is C_{11}. The assignment of singlets at 2·1 and 3·11 ppm would then be consistent with the presence of a C_9 methine and a C_{12} methylene. The hydroxyl group of physanol A was, therefore placed at C_{11}: the 11β-configuration would make this hydroxyl group too highly hindered to be easily acetylated. The ready acetylation of physanol A suggested that the hydroxyl group had an α-configuration. Moreover, the methine proton adjacent to the hydroxyl group appeared as a doublet (*J*10 Hz) of multiplets, indicating that this proton could be β-axial. The adjacent hydroxyl group should, therefore, be α-equatorial.

Since the debenzoylated products of physanol A did not form an acetonide and were also inert to the action of sodium periodate, these compounds were not 1,2 diols. The PMR spectrum of physanol A had a broad unresolved multiplet at 4·66 ppm due to a proton adjacent to the benzoyloxy group but in the spectra of the debenzoylphysanol A and A_1 this signal shifted upfield to 3·18 ppm. The position and shape of this methine multiplet is very characteristic of 2β-axial or 3α-axial protons of 2α or 3β hydroxy steroids respectively.[12] In view of the ubiquitous presence of an oxygen function at C_3 in natural steroids, the benzoyloxy group was located at the 3β-position.

The placement of functional groups in physanol A was further confirmed by calculating the shift values of 18- and 19-methyl groups of physanol A and its various derivatives*

* The additive shift contribution of 3β-benzoyloxy group was obtained from the difference in chemical shifts of 19- and 18-methyl groups of β-sitosterol, stigmasterol, α-spinasterol and those of the corresponding benzoates. The shift contribution of $^{2(3)}$bond was obtained by subracting the 19- and 18-methyl chemical shifts of dihydrophysanol A from those of physanol A. Other shift values were taken from literature.

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[11] BHACCA, N. S. and WILLIAMS, D. H. (1964) *Application of N.M.R. Spectroscopy in Organic Chemistry*, p. 66, Holden-Day, San Francisco.

[12] BRIDGEMAN, J. E., CHERRY, P. C., CLEGG, A. S., EVANS, J. M., JONES, E. R. H., KASAL, A., KUMAR, V., MEAKINS, G. D., MORISAWA, Y., RICHARDS, E. E. and WOODGATE, P. (1970) *J. Chem. Soc. C*, 250.

taking 5α-stigmastane[13] as the basic skeleton and comparing these values with the corresponding observed values. The calculated values were found to be in excellent agreement with the observed values. Structure **1** was therefore assigned to physanol A and since debenzoylphysanol A was the normal product of saponification of physanol A, its structure should be **2**. In debenzoylphysanol A_1 the enone (Δ^7, 6-oxo) double bond had migrated to a tetrasubstituted position $\Delta^{8(9)}$ or $\Delta^{8(14)}$.

Jones oxidation of debenzoylphysanol A yielded a 3,6,11-triketoproduct $C_{29}H_{42}O_3$ (M^+ 438). In the case of a $\Delta^{8(9)}$ bond, oxidation was expected to give the $\Delta^{8(9)}$ 11-oxo enone. The triketo product did not show an enone UV absorption, indicating that the tetrasubstituted double bond was situated at the $\Delta^{8(9)}$ position. A $\Delta^{8(9)}$ bond would have also rendered the splitting pattern of the 11-β-proton signal different from that in the PMR spectrum of physanol A. The pattern of this signal was, however, unchanged thus supporting the $\Delta^{8(14)}$ location of the double bond. The shifting of the physanol A conjugated double bond to the $\Delta^{8(14)}$ position is not entirely unexpected as migration to the $\Delta^{8(14)}$ position would stabilize ring D by relieving some of the strain inherent in a five membered ring. Structure **3** was, therefore assigned to debenzoylphysanol A_1.

Physanol A constitutes the first example of a steroid with a Δ^{20} bond isolated from a natural source. It is also the first example of a natural stigmastane compound having an 11-oxygen function.

Physanol B, $C_{36}H_{52}O_4$ (M^+ 548) also formed a monoacetate, $C_{38}H_{54}O_5$ (M^+ 590), and a monobenzoate $C_{43}H_{56}O_5$ (M^+ 652). The IR and PMR spectra were found to be similar to those of physanol A except for the absorptions due to vinylidene group.

The MW of physanol B indicated that it had one less double bond than physanol A. Its MS displayed a prominent peak *m/e* 285 formed by the loss of 141 a.m.u. from the (M^+–C_6H_5COOH) peak, representing the elimination of a saturated side chain. The identity of physanol B with dihydrophysanol A was established by their superimposable IR, mixed melting point and TLC. Physanol B, therefore, has structure (**4**).

EXPERIMENTAL

IR, UV and 60 MHz NMR spectra were recorded in KBr, EtOH and $CDCl_3$ with TMS as internal standard, respectively and $[\alpha]_D^{30}$ in $CHCl_3$. Silica gel was used for TLC with C_6H_6–MeOH (98:2) (A) and (92:8) (B), as solvents. Materials were visualized by spraying with 1% ceric sulphate in 2 N H_2SO_4.

The air-dried, powdered seeds (15 kg) from *Physalis franchetii* fruit were exhaustively extracted with C_6H_{14} and the extract concn under red. pres. On cooling (8°) for 7 days the concentrate deposited a white crystalline mass, which was filtered and thoroughly washed with C_6H_{14}. TLC(A) of this crude product (8 g) showed that it was a mixture of three major components A, B and C having R_f values of 0·51, 0·35 and 0·12 respectively. The mixture was chromatographed over neutral alumina 400 g (activity-3). Compound A was eluted with C_6H_{14}–C_6H_6 (1:1) and crystallized from $CHCl_3$–MeOH as colourless needles m.p. 234–6° (4·5 g). Compound B was largely eluted with C_6H_6 and C_6H_6–$CHCl_3$ (1:1). It also crystallized in colourless needles from $CHCl_3$–MeOH m.p. 232–3° (1·1 g).

The material eluted with C_6H_6–$CHCl_3$ (1:1) yielded compound C, (0·55 g), m.p. 136–37°, $[\alpha]_D$ −30°, identified as β-sitosterol by comparison and mixed m.p. of acetate.

Compound A (*physanol A*) crystallized from $CHCl_3$–MeOH as colourless needles m.p. 234–36, $[\alpha]_D$ +60. It gave a positive Liebermann–Burchard test; λ_{max}: 237 nm (ε 21 380); ν_{max} 3560, 3075, 3030, 2989, 2865, 1720, 1680, 1627, 1604, 1585, 1462, 1425, 1388, 1319, 1276, 1216, 1196, 1174, 1104, 1066, 1043, 1028, 1005, 988, 973, 893, 863, 842, 700 cm^{-1}; PMR; ppm 0·65, 0·93, (3H each, *s*, 2 quaternary CH_3); 1·07, 1·09, (3H, each, *d*, *J* 7 Hz, 2 secondary CH_3) 3·78, (1H *dm*, *J* 10, –CH–OH); 4·66 (1H, *m*, –CH–$OCOC_6H_5$) 4·86 and 4·95 (2, 1H, broad *s*, C=CH_2) 5·73 (1H, *q*, *J* 1·5 Hz, –C=CH–CO); 8·1 and 7·53 (2H, *dd*, *J* 7 and 2 Hz and 3H, *m*, respectively C_6H_5). Found: C, 79·07,

[13] BHACCA, N. S. and WILLIAMS, D. H. (1964) *Application of N.M.R. Spectroscopy in Organic Chemistry*, p. 13, Holden-Day, San Francisco.

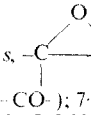
[14] ELIEL, E. L. (1962) *Sterochemistry of Carbon Compounds*, p. 266. McGraw-Hill, New York.

H, 9·32; $C_{36}H_{50}O_4$ requires: C, 79·1; H, 9·1%; Mass M^+ 546. Other ions M^+ 424 (M^+-122), 285 (M^+-122-139), 243 (265–42).

Mono-O-acetylphysanol A. Physanol A (75 mg) was allowed to stand 16 hr with dry C_6H_5N 0·5 ml) and Ac_2O (0·5 ml). The reaction product was purified by column chromatography over neutral alumine. It crystallized from $CHCl_3$–MeOH as colourless needles, m.p. 204–5°, $[\alpha]_D$ 42; ν_{max} 2950, 2862, 1725, 1708, 1680, 1630, 1594, 1572, 1450, 1378, 1322, 1310, 1272, 1196, 1179, 1140, 1110, 1068, 1030, 1000, 965, 935, 923, 895, 863, 820, 708, cm^{-1}. PMR, ppm 0·621, 0·93 (3H each *s*, quaternary CH_3) 1·05 (6H, *d*, *J* 7 Hz, 2 secondary CH_3), 2·0 (3H, *s*, $OCO.CH_3$) 4·76 (1H, broad *m*, $-CH-O.COC_6H_5$) 4·85, 4·91 (1H, each, *s*, $C=CH_2$) 5·25 (1H, *td*, *J* 6 and 2·5 Hz, $CH-OAc$); 5·83 (1H, *q*, *J* 1·5 Hz, $-C=CH-CO$), 8·25, 7·68 (2H, *dd*, *J* 7 and 2 Hz; 3H, *m* respectively, C_6H_5) Found: C, 77·42, H, 9·01, $C_{38}H_{52}O_5$ requires: C, 77·55; H, 8·84%; M^+ 588.

Oxidation of physanol A. Physanol A (100 mg) was dissolved in Me_2CO and 8 N chromic acid (Jones' reagent) added dropwise until an orange colour persisted. After standing for 10 min, Me_2CO was removed and the residue was diluted with H_2O and extracted with Et_2O. The Et_2O soln was washed with 5% $NaHCO_3$ and then with H_2O, dried and evaporated. The oxidation product (80 mg) was purified by silica gel chromatography using C_6H_6 as the eluant. The purified product crystallized from $CHCl_3$–MeOH as colourless needles (40 mg), m.p. 185–86, $[\alpha]$ +25, R_f (B) 0·32, λ_{max}: 234 nm (ε, 19, 040) ν_{max}: 2950, 1708, 1669, 1630, 1598, 1450, 1380, 1330, 1314, 1275, 1220, 1200, 1180, 1115, 1095, 1068, 1028, 973, 895, 869, 700 cm^{-1}; PMR: ppm 0·56, 0·88 (3H each *s*, 2 quaternary CH_3); 1·05 (6H, *d*, *J* 7 Hz, 2 secondary CH_3); 2·1 (1H, *s*, $CH-CO$) 3·11 (2H, *s*, $-CO-CH_2$), 4·68 (1H, *m* $-CH-O-CO-C_6H_5$), 4·76, 4·95 (1H each *s*, $C=CH_2$), 5·65 (1H, *q*, *J* 1·5 Hz, $C=CH-CO$) 7·3–7·56, 8·5–8·11 (3H and 2H respectively, $-C_6H_5$) Found: C, 79·35; H, 9·19; $C_{36}H_{48}O_4$ requires: C, 79·41; H, 8·82%, M^+ 544.

Epoxidation of physanol A. Physanol A (160 mg) was dissolved in $CHCl_3$ (15 ml), *m*-chloroperbenzoic acid (180 mg) added and the reaction mixture allowed to stand 16 hr. Excess *m*-chloroperbenzoic acid was destroyed by dropwise addition of a soln of Na metabisulphite and the reaction mixture washed with H_2O, dried and evaporated to dryness. The residue (160 mg) showed one major spot on TLC (A) and was purified by prep. TLC. The lower zone crystallized from $CHCl_3$–MeOH m.p. 225–30; ν_{max}: 3584, 2967, 2882, 1725, 1688, 1647, 1621, 1604, 1468, 1391, 1368, 1340, 1323, 1276, 1225, 1206, 1185, 1157, 1110, 1071, 1046, 1032, 1011, 979, 976, 931, 876, 848, 784, 709, 686 cm^{-1}; PMR: ppm 0·63 0·93 (3H each, *s*, 2 quaternary CH_3); 1·08 (2, 6H, *d*, *J* 7 Hz 2 secondary



CH_3); 2·68 (2H, *s*, $-C-CH_2$); 4·0 (1H, *dm*, *J* 10 Hz, $CH-OH$); 4·76 (1H, *m* $CH-OCOC_6H_5$); 5·76 (1H, *q*, *J* 1·5 Hz, $C=CH-CO-$); 7·3–7·71, 8·1–8·35 (3H and 2H respectively C_6H_5); Found: C, 76·79; H, 8·91; $C_{36}H_{50}O_5$ requires: C, 76·86; H, 8·89%; M^+ 562.

Catalytic hydrogenation of physanol A. Physanol A (300 mg) was dissolved in HOAc (200 ml) and hydrogenated in the presence of Pt catalyst for 8 hr. The reaction mixture was filtered and freed of HOAc at 50° under red. pres. The residue (290 mg) showed two spots on TLC R_f 0·4 and 0·12 (0·8% MeOH in C_6H_6). The products were separated by prep.-TLC (1·4% MeOH in C_6H_6). The product R_f 0·4 (30 mg) on crystallization furnished tetrahydrophysanol A, m.p. 128° (25 mg). ν_{max} 3401, 2907, 1710, 1458, 1387, 1118, 1276, 1256, 1199, 1182, 1138, 1116, 1071, 1037, 991, 971, 874, 714 cm^{-1}; PMR: ppm 0·75, 0·90 (3H each, *s*, 2 quaternary CH_3); 3·9 (1H, *dm*, *J* 10 Hz, $CH-OH$) 4·6 (1H, *m*, $CH-O.CO-C_6H_5$) 7·5–7·8, 8·1–8·35 (3H and 2H respectively, C_6H_5) Found: C, 78·49; H, 10·01; $C_{36}H_{54}O_4$ requires: C, 78·54; H, 9·81%, M^+ 550.

The other reaction product, R_f 0·12 (250 mg) crystallized as needles from $CHCl_3$–MeOH and proved to be dihydrophysanol A, (220 mg) m.p. 232–33°; $[\alpha]_D$ +68°, λ_{max} 235 nm; ν_{max}: 3480, 3035, 3010, 2985, 2860, 1720, 1680, 1650, 1604, 1580, 1460, 1380, 1332, 1318, 1276, 1225, 1211, 1192, 1122, 1112, 1076, 1032, 1009, 979, 935, 872, 843, 829, 813, 714 cm^{-1}. PMR: 0·62, 0·93 (3H each, *s*, 2 quaternary CH_3); 3·65 (1H, *dm*, *J* 10 Hz, $CH.OH$) 4·78, (1H, *m*, $CH-O-COC_6H_5$); 5·8 (1H, *q*, *J* 1·5 Hz, $C=CH-CO-$) 7·65–7·81, (3H, *m* and 2H *dd*, *J* 7 and 2 Hz respectively, C_6H_5). Found: C, 78·67, H, 9·47; $C_{36}H_{52}O_4$ requires: C, 78·83; H, 9·48%; M^+ 548. Hydrogenation of physanol A in EtOAc in the presence of Pt catalyst for 6 hr, furnished only dihydrophysanol A.

Hydrolysis of physanol A. Physanol A (300 mg) was stirred in 0·2 M KOH in MeOH (25 ml) at 20° for 48 hr. The reaction mixture was diluted with H_2O (10 ml), MeOH removed under red. press. and the aq. soln extracted with Et_2O. The Et_2O layer was washed 3× with dil. HCl, then with 5% $NaHCO_3$ and finally with H_2O. Removal of solvent yielded a neutral product. The aq. alkaline phase was acidified with dil. HCl and extracted with Et_2O. The Et_2O extract was washed with H_2O, dried and evaporated. The acidic residue crystallized from H_2O m.p. 121–22°. It was identified as benzoic acid by mixed mp. with an authentic sample and comparison of IR and TLC. The neutral product showed two spots on TLC (B) R_f 0·24 and 0·36 designated debenzoylphysanol A and debenzoyl physanol A_1 respectively. The neutral mixture (250 mg) was chromatographed over neutral alumina (18 g). Debenzoylphysanol A_1 was eluted with C_6H_6–$CHCl_3$ (1:1) and debenzyol physanol A largely with C_6H_6–$CHCl_3$ (1:3), m.p. 210–11° (120 mg).

Debenzoylphysanol A crystallized from MeOH; m.p. 208–9°; λ_{max}: 245 nm. (12, 250); ν_{max}, 3533, 3250, 2950, 1670, 1633, 1488, 1383, 1300, 1200, 1140, 1050, 997, 980, 890, 870, 770 cm^{-1}; PMR: ppm 0·63, 0·86 (3H, each, *s*, 2 quaternary CH_3); 1·05, 1·06 (3H each *d*, *J* 7 Hz, 2 secondary CH_3) 3·18 (1H, *m*, $-CHOH$); 3·85 (1H, *dm*, *J* 10 Hz, $CHOH$); 4·93, 5·03 (1H each, *s*, $C=CH_2$); 5·76 (1H *q* *J* 1·5 Hz, $C=CH-CO-$). Found C, 65·59; H, 10·51, $C_{29}H_{46}O_3$ required: C, 65·61; H, 10·4%; M^+ 442.

Debenzoylphysanol A_1 crystallized from C_6H_{14}–MeOH; m.p. 210–11°; λ_{max}: 208 nm (ε, 8, 142); ν_{max}: 3445, 3250, 2933, 1708, 1638, 1467, 1389, 1310, 1248, 1212, 1187, 1050, 998, 970, 930, 897, 650, 604 cm^{-1}; PMR: ppm 0·64, 0·90 (3H each *s*, 2 quaternary CH_3); 1·06, 1·1 (3H each, *d*, *J*7 Hz, 2 secondary CH_3); 3·0 (2H narrow *m*, –C=C CH_2–CO); 3·20 (1H, *m*, –CHOH); 3·86 (1H, *dm*, *J*10 Hz, –CHOH); 4·9, 5·0 (1H each, *s*, C=CH_2); Found: C, 65·58; H, 10·49; $C_{29}H_{46}O_3$ requires: C, 65·61, H, 10·4%; M^+ 442.

Oxidation of debenzoylphysanol A_1. Debenzoylphysanol A_1 (80 mg) was dissolved in Me_2CO and 8 N chromic acid added dropwise until an orange colour persisted. After 10 min at 20° Me_2CO was removed, the residue diluted with H_2O and extracted with Et_2O. The Et_2O soln was washed with 5% $NaHCO_3$ H_2O, dried and evaporated. The residue crystallized from MeOH, m.p. 191°. λ_{max}: 217 nm. ν_{max}, 2960, 2806, 1711, 1633, 1456, 1383, 1360, 1325, 1248, 1210, 1053, 1010, 973, 892 cm^{-1}. PMR: ppm 0·87, 1·12 (3H each, *s*, 2 quaternary CH_3) 3·03 (2H, *m*–C–CH_2CO–) 3·23 (2H, *s*, –CO–CH_2); 4·88, 5·05 (1H each, *s*, –C=CH_2). Found: C, 66·19; H, 9·41 $C_{29}H_{42}O_3$ requires: C, 66·21; H, 9·36% M^+ 438.

Compound B (*Physanol B*). Physanol B crystallized from $CHCl_3$–MeOH as colourless needles, m.p. 232–33°. It gave a positive Liebermann–Burchard test; λ_{max}: 235 nm, ν_{max}: 3480, 3035, 3010, 2985, 2860, 1720, 1680, 1630, 1604, 1580, 1460, 1380, 1276, 1112 1076, 1032, 1010, 979, 925, 872, 714 cm^{-1}, PMR ppm 0·62, 0·91 (3H each, *s*, 2 quaternary CH_3); 1·07, 1·08 (3H each, *d*, *J*7 Hz 2 secondary CH_3); 3·65 (1H, *dm*, *J*10 Hz, –CH–OH), 4·78 (1H broad *m*, CH–OCO–); 5·81 (1H, *q*, *J*1·5 Hz, –C=CH–CO); 7·53, 8·1 (3H, *m*, and 2H, *dd*, *J*7 and 2 Hz respectively, C_6H_5). Found: C, 78·79; H, 9·47; $C_{36}H_{52}O_4$ requires: C, 78·83 H, 9·49%; M^+ 548. Other ions M^+ 426 (M^+–122), 285 (M^+–122–141), 243 (285–42).

Mono–O–acetylphysanol B. Physanol B (80 mg) in dry C_5H_5N (0·5 ml) and Ac_2O (0·5 ml) was allowed to stand 16 hr. The reaction product was purified by chromatography on neutral alumina and crystallized from $CHCl_3$–MeOH m.p. 232°; ν_{max}: 2967, 2924, 1730, 1724, 1689, 1647, 1621, 1604, 1462, 1397, 1340, 1280, 1252, 1211, 1192, 1151, 1119, 1082, 1035, 981, 876, 830, 817, 717, 692 cm^{-1} PMR: ppm 0·62, 0·93 (3H each *s*, 2 quaternary CH_3); 2·05 (3H *s*, –OCOCH_3) 4·76 (1H broad *m*, –CH–OCOC_6H_5), 5·1 (1H, *dm*, *J*10 Hz, –CH–OAC); 5·78 (1H, *q* *J*1·5 Hz, –C=CH–CO–); 8·15, 7·58 (2H, *dd* *J*7 and 2 Hz, 3H, *m*, respectively C_6H_5), Found: C, 77·19; H, 9·22; $C_{38}H_{54}O_5$ requires: C, 77·28; H, 9·15%; M^+ 590.

Mono–O–benzoylphysanol B. Physanol B (60 mg) was treated with PhCOCl (0·5 ml) in dry C_5H_5N (0·5 ml) and the reaction mixture was allowed to stand 16 hr. The product was purified by chromatography on neutral alumina and crystallized from $CHCl_3$–MeOH m.p. 230–31°, ν_{max}: 2967, 2882, 1727, 1698, 1684, 1642, 1621, 1604, 1458, 1397, 1326, 1280, 1229, 1192, 1119, 1080, 1035, 981, 876, 716, 692 cm^{-1} PMR: ppm 0·63, 0·93 (3H each, *s*, 2 quaternary CH_3) 4·78 (1H, *m*, CH–OCOC_6H_5); 5·78 (1H *q*, *J*1·5 Hz, –C=CH–CO–); 5·35 (1H, *dm*, *J*10 Hz, –CH–O–CO–C_6H_5); 7·51–7·8, 8·05–8·35 (6H and 4H respectively 2 C_6H_5). Found: C, 79·06; H, 8·84; $C_{43}H_{56}O_5$ requires: C, 79·14; H, 8·58%; M^+ 652.