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TERPENOIDS—LXXV

CONSTITUENTS OF NARDOSTACHYS JATAMANSI AND SYNTHESIS OF (±) DIHYDROSAMIDIN AND VISNADIN FROM JATAMANSIN*

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Abstract—In continuation of the examination of the oil from the roots of *Nardostachys jatamansi* several hydrocarbons, a new oxide, alcohols, a polyoxygenated crystalline material together with β-eudesmol, elemol, β-sitosterol, angelicin and jatamansinol, have been isolated. Jatamansin has been converted into the vasodilatory agents, dihydrosamidin and visnadin.

IN AN earlier communication[1] dealing with the examination of the chemical constituents of *Nardostachys jatamansi* (greyish brown variety of Indian origin), we have reported the isolation of oroselol and the new terpenic coumarin jatamansin (I). The structure of the latter was established by chemical degradation, UV, IR and NMR spectral studies.†

In addition, we now have been able to isolate several hydrocarbons, a new oxide, alcohols, a polyoxygenated crystalline material, together with β-eudesmol, elemol (II),[4] β-sitosterol, angelicin (III)[5] and the alcohol jatamansinol (IV, 3′-hydroxy-3′,4′-dihydroseselin) which is also obtained by the hydrolysis of jatamansin with alkali. Jatamansinol is identical with lomatin, which has been obtained by Soine from *Lomatium nuttallii* (A. Gray).[3]

Recently we converted jatamansinol (IV) into dihydrojatamansin (V) by

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† This product (named selinidin) was subsequently isolated by Seshadri *et al.* from *Selinum vaginatum*.[2] The optical rotation of this compound as reported by them in dioxan is opposite to that of jatamansin in chloroform. Suspecting that stereochemical factors may be involved, all the rotations were checked again in different solvents. It was found that, this apparent discrepancy was due to the effects of solvents only. Following are the sp. rotations of some of the products in different solvents.

Compound	Chloroform	Ethanol	Dioxan
Jatamansin	−24·06°	+8·6°	+1·5°
Selinidin[2]	—	—	+20·3°
Jatamansinol	+7·6°	+56·9°	+35·56°
Selinetin[2]	—	—	+17·2°
Lomatin[3]	—	+74·8°	—

[1] S. N. Shanbhag, C. K. Mesta, M. L. Maheshwari, S. K. Paknikar and S. C. Bhattacharyya, *Tetrahedron* **20**, 2605 (1964).

[2] T. R. Seshadri, M. S. Sood, K. L. Handa and Vishwapaul, *Tetrahedron Letters* No. 45, p. 3367 (1964).

[3] T. O. Soine and F. H. Jawad, *J. Pharm. Sc.* **53**, 990 (1964).

[4] A. M. Clover, *Phillipine, J. Sc.* **2A** 1 (1907); K. Kafuku, T. Ikeda and Y. Fujita, *J. Chem. Soc., Japan* **53**, 636 (1932).

[5] A. Chatterjee and S. Sen Gupta, *Tetrahedron Letters* No. 29, 1961 (1964).

esterification[6] with α-methyl butyroyl chloride and found that both the products, synthetic as well as the one obtained by hydrogenation of jatamansin (I), are identical in all respects.

Jatamansin (I) is closely related to the active vasodilatory drugs, visnadin (VIa), samidin (VIb), dihydrosamidin (VIc)[7,8] pteryxin (VIIa) and suksdorfin (VIIb).[9] In the first paper of this series[1] we determined the structure of jatamansin, but its stereochemistry was left unsolved. In order to decide its stereochemistry and also to convert it into the known vasodilatory agents mentioned above, a series of experiments were undertaken and the results are reported in the present communication.

In an attempt to introduce an acetoxy group in the 4′ position, dihydrojatamansin (V) was treated with lead tetra-acetate[10] under various conditions but in every case V was recovered unchanged. Other oxidizing agents, mercuric acetate, chromic acid and selenium dioxide[11] also failed. This inactivity is probably due to the steric effect of the flexible, overlapping ester side chain in dihydrojatamansin. Similarly, jatamansinol (IV) and the corresponding acetate could not be oxidized with lead tetra-acetate or other oxidising reagents.

Consequently, jatamansinol (IV) was oxidized to jatamansinone (VIII, (±)-3′-keto-3′,4′-dihydroseselin), during which optical activity of the secondary hydroxyl group was lost and subsequent experiments for determining the absolute stereochemistry of jatamansinol and jatamansin were useless.

The use of excess of Jones' reagent[12] during the oxidation of jatamansinol (IV) gave only poor yields of jatamansinone (VIII), together with substantial amounts of the diketone (IX) and acidic components. Yields of VIII could be improved by using the required amount of the reagent and working up the reaction product immediately.

The ketone (VIII) on treatment with lead tetra-acetate[10] furnishes the keto-acetate (X, (±)-3′-keto-4′-acetoxy-3′,4′-dihydroseselin). However, under normal conditions the yield of the keto-acetate (X) was low and several by-products were formed simultaneously. The method therefore was modified by performing the oxidation at room temperature under an atmosphere of nitrogen, resulting in better yields of the ketoacetate (X) and the formation of a new compound, m.p. 215°, which has not been characterized.

Reduction of the keto-acetate (X) with sodium borohydride[13] under various conditions yielded the (±)-mono acetyl khellactone (XI, (±)-3′-hydroxy-4′-acetoxy-3′,4′-dihydroseselin).[7,8] Better yields of XI were obtained by carrying out the reduction in dioxan[14] for ½ hr at 2–5°. A small amount of (±)-khellactone (XII, (±)-3′,4′-dihydroxy-3′,4′-dihydroseselin) was also formed.

[6] R. E. Willette and T. O. Soine, *J. Pharm. Sc.* **53**, 275 (1964).
[7] E. Smith, N. Hosansky, W. G. Bywater and E. E. van Tamelen, *J. Amer. Chem. Soc.* **79**, 3534 (1957).
[8] H. D. Schroeder, W. Bencze, O. Halpern and H. Schmid, *Chem. Ber.* **92**, 2388 (1959).
[9] R. E. Willette and T. O. Soine, *J. Pharm. Sc.* **51**, 149 (1962).
[10] W. S. Johnson, A. D. Kemp, R. Pappo, J. Ackerman and W. F. Johns, *J. Amer. Chem. Soc.* **78**, 6312 (1956); L. F. Fieser and R. Stevenson, *Ibid.* **76**, 1728 (1954); G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.* 3943 (1954).
[11] K. B. Wiberg and S. D. Nielsen, *J. Org. Chem.* **29**, 3353 (1964).
[12] A. Bowers, T. G. Halsall, E. R. H. Jones and A. J. Lemin, *J. Chem. Soc.* 2555 (1953).
[13] E. Elisberg, H. Vanderhaeghe and T. F. Gallagher, *J. Amer. Chem. Soc.* **74**, 2814 (1952).
[14] A. Hunger and T. Reichstein, *Chem. Ber.* **85**, 635 (1952).

(±)-Dihydrosamidin (VIc), m.p. 125–127°, was obtained as a result of condensation of (±)-monoacetyl khellactone (XI) with isovaleroyl chloride.[6] Its structure is fully supported by its NMR spectrum (Fig. 1). In addition to dihydrosamidin, a small amount of a chlorocompound, (±)-3′-chloro-4′-acetoxy-3′,4′-dihydroseselin (XIII) was also obtained. This was possibly formed by the action of traces of PCl_3 present in the isovaleroyl chloride as a contaminant. The m.p. of (±)-dihydrosamidin obtained is higher than that of the naturally occurring (+)-*cis*-dihydrosamidin (m.p. 117–119°).[7] A similar behaviour has been observed by Schroeder *et al.*[8] during the preparation of (±)-*trans*-samidin (VIb, m.p. 149–150°; natural (+)-*cis*-samidin, m.p. 138–139°).

(±)-Visnadin (VIa), m.p. 150–152° was also prepared by condensation of (+)-monoacetyl khellactone (XI) with α-methyl butyroyl chloride following the above procedure. Natural (+)-*cis*-visanidin melts at 85–88°. The m.p. difference is very conspicuous in the present case, but the structure of the product is fully supported by analysis and NMR spectrum (Fig. 1).

The preparation of pteryxin (VIIa) and suksdorfin (VIIb) via the keto alcohol (XIV, 3′-keto-4′-hydroxy-3′,4′-dihydroseselin) will be undertaken in the near future.

EXPERIMENTAL

All m.ps are uncorrected. The b.ps unless otherwise stated correspond to bath temps. Rotations unless otherwise stated were taken in $CHCl_3$ solution. Neutral alumina, graded according to Brockmann scale[15] of activity was used in chromatography. Silica gel used for chromatography was activated by heating at 450° for 1 hr. The Pet. ether refers to the fraction b.p. 60–80°. The help received from our microanalytical, spectroscopy and gas chromatography sections is gratefully acknowledged.

Isolation. The pet. ether fraction (160 g) from the chromatography of jatamansi root oil was fractionally distilled and 2 fractions collected. The lower boiling fraction (b.p. 57–70°/15 mm, 90 g) contained mainly monoterpenes of which α-pinene, β-pinene and Δ^3-carene were characterized by GLC. The higher boiling fraction (110–230°/0·1 mm; 50 g) on repeated chromatography on alumina furnished, a mixture of sesquiterpene hydrocarbons (12 g) which could not be further separated by adsorption chromatography; a new oxide [500 mg, b.p. 120–125°/0·5 mm; IR bands at: 2985, 1600, 1504, 1466, 1403, 1377, 1362, 1346, 1255, 1235, 1209, 1181, 1149, 1114, 1099, 1070, 1050, 995, 862, 844, and 812 cm^{-1}. (Found: C, 79·36; H, 10·15%)]; a ketonic fraction (7 g) and a mixture of alcohols (27 g) which on further chromatography over $AgNO_3$-impregnated silica gel (15% $AgNO_3$)[16] gave a mixture of three alcohols (20·5 g); β-eudesmol (500 mg), m.p. 68–72°; $(\alpha)_D$ + 63·04° (*c*, 0·8); IR bands at: 3367, 3125, 2985, 1645, 1453, 1404, 1376, 1290, 1263, 1215, 1188, 1166, 1135, 1100, 1049, 1009, 985, 959·7, 909·9, 887, 857, 824·4, 793·7 and 769·2 cm^{-1}; mixed m.p. undepressed on admixture with an authentic specimen. (Found: C, 81·37; H, 11·77. Calc. for $C_{15}H_{26}O$: C, 81·02; H, 11·79%) and elemol (II, 5 g), m.p. 48–51°; $(\alpha)_D$ − 5·87° (*c*, 2·21); IR bands at: 3425, 3135, 3003, 1645, 1471, 1445, 1414, 1381, 1361, 1295, 1269, 1220, 1190, 1181, 1130, 1092, 1053, 1010, 965, 939, 914, 892, 847, 798 and 710·4 cm^{-1}; mixed m.p. with an authentic specimen undepressed. (Found: C, 80·61; H, 11·69. Calc. for $C_{15}H_{26}O$: C, 81·02; H, 11·79%.)

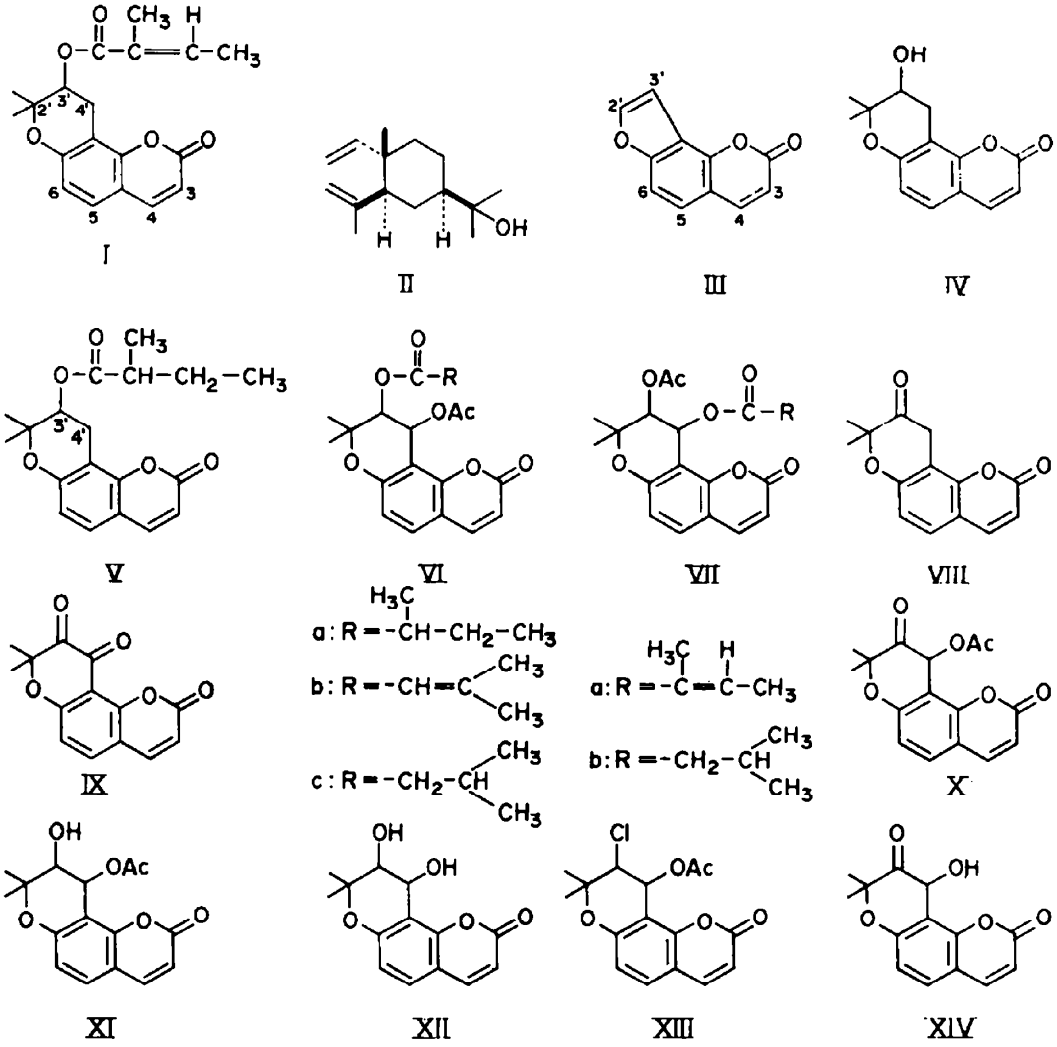
The residue (18 g) left after the distillation of above 2 fractions, was chromatographed several times over alumina to afford a semi solid long chain hydrocarbon, $C_{30}H_{62}$ (310 mg; b.p. 110–115°/$7·7 \times 10^{-3}$ mm, no colouration with tetranitromethane). (Found: C, 85·20; H, 14·30. Calc. for $C_{30}H_{62}$: C, 85·22; H, 14·78%); β-sitosterol (3 g), m.p. 135–137° was undepressed on admixture with an authentic specimen.

After the separation of jatamansin (I)[1] from the benzene fraction (850 g) after chromatography of

[15] H. Brockman and F. J. McQuillin, *J. Chem. Soc.* 2423 (1955); E. Lederer and M. Lederer *Chromatography* p. 26. Elsevier, N.Y. (1957).

[16] P. Teisseire, *Recherches* 14, 81 (1964).

CHART I



jatamansi oil (2 kg), the latter eluates, on further chromatography on Gr. III alumina, furnished angelicin (an unknown crystalline polyoxygenated compound) and jatamansinol respectively.

Angelicin III. (300 mg), m.p. 137–138° has IR bands at: 2941, 1724, 1709, 1613, 1513, 1399, 1370, 1333, 1266, 1250, 1147, 1119, 1055, 1038, 999, 833 and 747 cm^{-1}; UV spectrum: λ_{max} 297 and 245 mμ (log ε 3·96 and 4·38 respectively); NMR spectrum (in acetone): a pair of doublets at τ = 1·97 (1H) and 3·62 (1H), J = 9 c/s (due to protons at 4 and 3 respectively); another pair of doublets at τ = 2·04 (1H) and 2·87 (1H), J = 2 c/s (due to protons at 2′ and 3′ respectively) and a strong singlet at τ = 2·48 (2H), due to protons at 5 and 6); it did not depress the m.p. of an authentic sample of angelicin.* (Found: C, 70·79; H, 3·69. Calc, for $C_{11}H_6O_3$: C, 70·97; H, 3·25%.)

* We are indebted to Prof. (Mrs) A. Chatterjee for supplying the sample of angelicin.

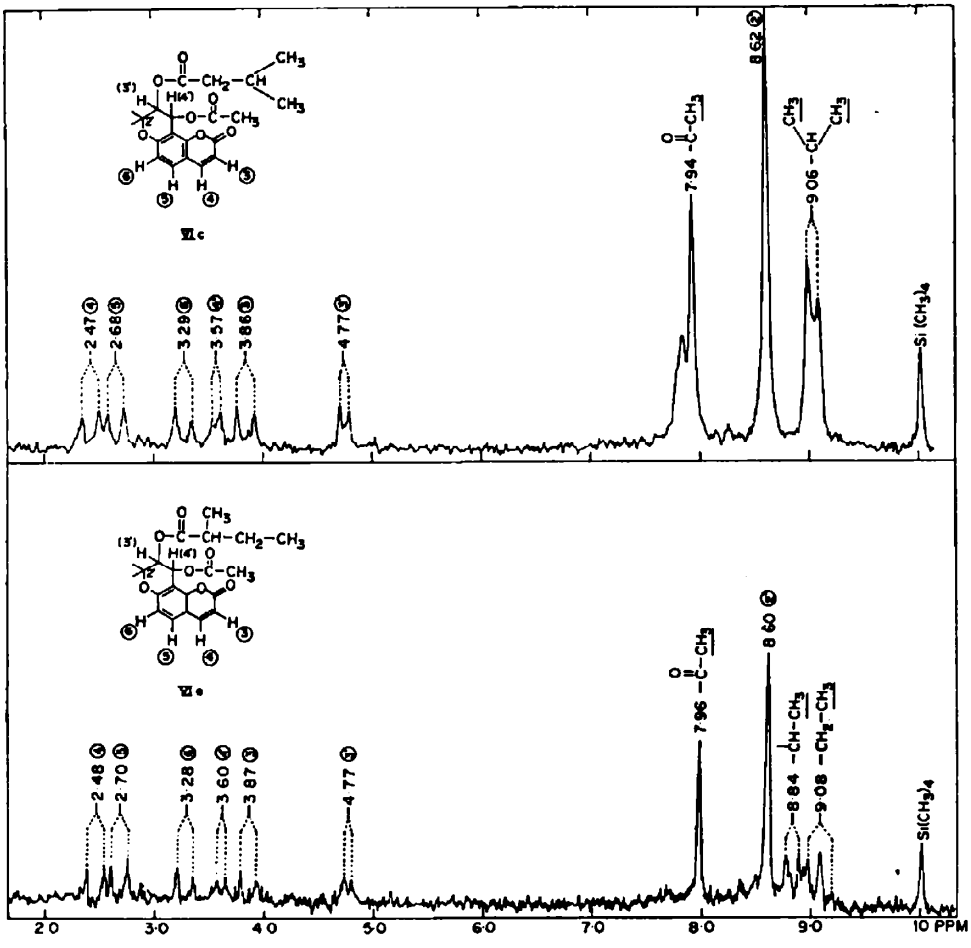


FIG. 1

Unknown polyoxygenated compound (7 g), m.p. 77–78° $(\alpha)_D$ − 252° (*c*, 5·8) has UV spectrum: λ_{max} 216 mμ (ε 10,732); IR bands at: 3546, 1724, 1664, 1637, 1370, 1344, 1263, 1221, 1147, 1105, 1081, 1031, 1015, 991, 967, 934, 917, 851, 822 and 754 cm^{-1}.

Jatamansinol (IV; 4·2 g), m.p. 182–183°; $(\alpha)_D$ + 55·12° (*c*, 1·02, EtOH) was undepressed on admixture with an authentic specimen of jatamansinol obtained from hydrolysis of jatamansin. The IR and UV spectra are identical with those of an authentic sample. (Found: C, 68·55; H, 5·84. Calc. for $C_{14}H_{14}O_4$: C, 68·28; H, 5·73%.)

Preparation of dihydrojatamansin (V). A suspension of jatamansinol (IV, 930 mg) in dry benzene (25 ml) was added to α-methyl butyroyl chloride (460 mg) in dry benzene (15 ml). The mixture, protected by a $CaCl_2$ guard tube, was refluxed on a steam bath for 24 hr. The course of the reaction was followed by TCL on silicic acid. The reaction mixture was cooled, diluted with benzene (50 ml), washed with $NaHCO_3$ aq and then with water. The benzene solution was dried over Na_2SO_4, and the solvent removed to afford a residue (1·2 g), which on chromatography over Gr. II alumina (25 g) gave dihydrojatamansin (V, 1 g, in 300 ml benzene elution). This recrystallized from pet. ether in colourless crystals, m.p. 107–108°, $(\alpha)_D$ + 9·5° (*c*, 4·1). Its m.p. remained undepressed with an authentic specimen, obtained by hydrogenation of jatamansin* (I). Its IR, UV and NMR spectra

* In our earlier communication[1] m.p. of dihydrojatamansin has been reported as 100–101°, but now after repeated crystallizations in pet. ether, it is 107–108°.

were identical with those of an authentic sample. (Found: C, 69·32; H, 6·98. Calc. for $C_{18}H_{22}O_5$: C, 69·07; H, 6·71%.)

Preparation of jatamansinone (VIII). Jatamansinol (IV, 13 g) was dissolved in acetone (250 ml) in a 500 ml, 3-necked round bottom flask fitted with a thermometer, a dropping funnel and a mechanical stirrer. The solution was cooled in an ice salt mixture. Jones' reagent[18] (26 ml) was added slowly (1/2 hr) with stirring. Excess of the reagent was destroyed immediately with MeOH until the mixture became green. The solvents, acetone and MeOH were removed. The residue was then extracted with ether 4 times. The ethereal extract was washed with $NaHCO_3$ aq, water, then dried (Na_2SO_4) and the solvent removed to give a residue (12·3 g). The neutral residue was chromatographed over silica gel (20 times); elution with benzene–ether mixture (75:25, 150 ml) gave jatamansinone (5·9 g) and ether (500 ml) gave unreacted jatamansinol (6·3 g). Jatamansinone was recrystallized from ethyl acetate to give an analytical sample m.p. 157–158°, having all other constants in agreement with those reported earlier.[1] (Found: C, 68·89; H, 4·83. Calc. for $C_{14}H_{12}O_4$: C, 68·84; H, 4·95%.)

Sodium bicarbonate washings of the above reaction product, on acidification, extraction with ether, washing with water, drying (Na_2SO_4) and removal of solvent afforded an acidic residue (614 mg).

With a view to getting better yields of jatamansinone (VIII), the above reaction was repeated with excess Jones' reagent and prolonged stirring time (2–3 hr). After working up in the usual way, it was found that from 11·3 g jatamansinol 3 g of an acidic portion, 100 mg jatamansinone and 520 mg diketone were formed [chromatography of neutral portion over silica gel (20 times) gave jatamansinone in benzene–ether mixture (75:25, 35 ml), diketone in benzene ether mixture (50:50, 300 ml) and unreacted jatamansinol (7·2 g) in ether (500 ml)].

Diketone (IX). This compound has the following constants in agreement with those previously reported,[8] m.p. 268–270°, IR bands at: 1721, 1592, 1560, 1475, 1445, 1425, 1391, 1366, 1335, 1280, 1253, 1186, 1153, 1142, 1104, 1064, 992, 967, 943, 832·6 and 776·4 cm^{-1}.

Preparation of keto acetate (X). Lead tetra-acetate (9·40 g) was added to a solution of jatamansinone (VIII, 4·94 g) in acetic acid (120 ml) and the mixture stirred at room temp under an atmosphere of N_2 for 1 hr. The product was diluted with a large amount of water and extracted with ether, the ether extract was washed with water, $NaHCO_3$ aq and finally with water, dried over Na_2SO_4 and the solvent removed to furnish a residue (4·4 g). This on chromatography over silica gel (110 g) furnished unreacted jatamansinone (VIII, 1·0 g, elution with 200 ml–benzene); keto-acetate [X, 2·6 g elution with 400 ml benzene–ether mixture (93:7)] and an unknown compound [600 mg, elution with 200 ml benzene:ether (50:50) m.p. 215°]. The *keto acetate* (X) was recrystallized twice from benzene to give colourless crystals, m.p. 180–181°, $(\alpha)_D \pm 0°$; UV spectrum: λ_{max} 324 and 261 mμ (log ε 4·11 and 3·55 respectively; IR bands at: 2985, 1739, 1613, 1460, 1370, 1316, 1289, 1250, 1143, 1111, 1073, 1036, 985, 938, 893, 862, 843, 769 and 716 cm^{-1} (Found: C, 63·63; H, 4·98. $C_{16}H_{14}O_6$ requires: C, 63·57; H, 4·6%).

Preparation of (±) *mono-acetyl-khellactone* (XI). To a cooled (2–5°) stirred solution of the keto acetate (X, 1·3 g) in dioxan (80%, 110 ml), a solution of $NaBH_4$ (232 mg) in dioxan (10 ml) was added during a period of 5 min. The mixture was stirred for an additional 25 min at the same temp. The solution was made slightly acidic (pH 4–5) with 1N H_2SO_4 and concentrated under red. press. to 5 ml and then extracted with ether. The ether extract was washed with $NaHCO_3$ aq, water, dried over Na_2SO_4 and evaporated to give a residue (1·30 g) which was chromatographed over silica gel (32 g) to give monoacetyl khellactone [936 mg, elution with 200 ml benzene–ether mixture (70:30)] and khellactone (200 mg, elution with 50 ml, ether).

Monoacetyl khellactone (XI). This was purified by crystallization (twice) from benzene to furnish colourless crystals, m.p. 182–183°, $(\alpha)_D^{30} \pm 0°$, UV spectrum: λ_{max} 324, 261 and 249 mμ (log ε 4·14, 3·52 and 3·57 respectively) IR bands at: 3509, 1748, 1709, 1613, 1460, 1406, 1370, 1282, 1227, 1111, 1020, 971, 889, 833 and 766 cm^{-1} (Found: C, 62·95; H, 5·36. $C_{16}H_{16}O_6$ requires: C, 63·15; H, 5·30%).

Khellactone (XII). This was purified by crystallization (twice) from benzene to furnish colourless crystals, m.p. 156–158°, $(\alpha)_D^{30} \pm 0°$; IR bands at: 3401, 2941, 1727, 1686, 1605, 1486, 1453, 1395, 1366, 1348, 1285, 1241, 1179, 1159, 1136, 1114, 1092, 1053, 1020, 1000, 990, 925, 885, 847, 798, 775 and 747 cm^{-1}. (Found: C, 64·33; H, 5·65. $C_{14}H_{14}O_5$ requires: C, 64·11; H, 5·38%.)

Preparation of (±) *-dihydrosamidin* (VIc). A suspension of *monoacetyl khellactone* XI (134 mg) in dry benzene (10 ml) was added to a solution of isovaleroyl chloride (138 mg) in dry benzene (2 ml)

and the reaction carried out in a manner similar to the preparation of V from IV. The reaction product (160 mg), after working up in the customary manner, was chromatographed on silica gel (4 g).

Benzene-ether elution (97:3, 20 ml) afforded XIII (30 mg), which on crystallization from benzene gave colourless plates, m.p. 201–203°, $(\alpha)_D \pm 0°$; UV spectrum: λ_{max} 324 and 261 mμ (log ε 4·16 and 3·62 respectively); IR bands at: 2985, 1739, 1613, 1493, 1471, 1408, 1370, 1282, 1235, 1149, 1124, 1070, 1036, 1000, 955, 917, 840, 793, 757, and 694 cm^{-1}; NMR spectrum (in $CDCl_3$): a pair of doublets at τ — 2·4 (1H) and 3·75 (1H), J = 9 c/s (due to protons at 4 and 3 respectively) second pair of doublets at τ = 2·65 (1H) and 3·23 (1H), J = 8·5 c/s due to protons at 5 and 6 respectively), a third pair of doublets at τ = 4·63 (1H) and 4·79 (1H) J = 2·5 c/s (due to protons at 4′ and 3′ respectively), a singlet at τ = 7·99 (3H, due to —CO—CH_3 group) and two singlets at τ = 8·45 (3H) and 8·65 (3H, due to gemdimethyl group at 2′). (Found: C, 59·55; H, 4·54. Cl, 11·44. $C_{16}H_{18}O_6Cl$ requires: C, 59·44; H, 4·64; Cl, 10·97%).

Benzene-ether elution (93:7, 50 ml) furnished (+)-dihydrosamidin, which on crystallization from pet. ether gave colourless crystals (50 mg), m.p. 125–127°, $(\alpha)_D$ + 0°; UV spectrum: λ_{max} 324, 260 and 249 mμ (log ε 4·17, 3·57 and 3·65 respectively); IR bands at: 2985, 1754, 1613, 1494, 1471, 1410, 1379, 1299, 1235, 1190, 1124, 1053, 1030, 1010, 920, 893, 851, 836 and 778 cm^{-1}; NMR spectrum (Fig. 1, in CCl_4); doublets at τ = 2·47 (1H, J = 9 c/s, due to proton at 4), τ = 2·68 (1H J = 8 c/s, due to proton at 5) τ = 3·29 (1H, J = 8 c/s, due to one proton at 6), τ = 3·57 (1H, J = 5 c/s, due to one proton at 4′) τ = 3·86 (1H, J = 9 c/s due to one proton at 3), τ = 4·77 (1H, J = 5 c/s, due to proton at 3′), singlets at τ = 7·94 (3H, due to —OC—CH_3 group at 4′) and τ = 8·62 (6H, due to gem-dimethyl group at 2′), doublet at τ = 9·06 (6H, J = 6 c/s, due to —CH$\langle^{CH_3}_{CH_3}$ group). (Found; C, 64·86; H, 6·26. Calc. for $C_{21}H_{24}O_7$: C, 64·95; H, 6·23%).

Preparation of (±)-*visnadin* (VIa). (+)-Monoacetyl khellactone (XI, 150 mg) was esterified with α-methyl butyrol chloride (130 mg) by following the procedure described earlier. The reaction product was chromatographed on silica gel (6 g). Benzene-ether mixture (95·5, 60 ml) eluted crude visnadin (150 mg), which on crystallization (3 times) with pet. ether afforded VIa (60 mg), m.p. 150–152°, $(\alpha)_D \pm 0°$; IR bands at: 2941, 1739, 1608, 1486, 1458, 1372, 1348, 1277, 1229, 1181, 1147, 1103, 1062, 1007, 926, 909, 892, 846 and 775 cm^{-1}; NMR spectrum (Fig. 1; in CCl_4): doublets at τ = 2·48 (1H, J = 9 c/s, due to one proton at 4), τ = 2·70 (1H, J = 8 c/s, due to one proton at 5), τ = 3·28 (1H, J = 8 c/s, due to one proton at 6), τ = 3·60 (1H, J = 5 c/s, due to one proton at 4′) τ = 3·87 (1H, J = 9 c/s, due to one proton at 3), τ = 4·77 (1H, J = 5 c/s, due to one proton at 3′), singlets at τ = 7·96 (3H, due to OC—CH_3 group), at τ = 8·60 (6H, due to gem-dimethyl group at 2′); a doublet at τ = 8·84 (3H, J = 7 c/s due to CH_3—CH grouping) and a triplet at τ = 9·08 (3H, due to CH_3—CH_2— grouping). (Found: C, 65·16; H, 6·44. Calc. for $C_{21}H_{24}O_7$: C, 64·95; H, 6·23%).