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TERPENOIDS—XCV

SYNTHESIS OF (±)-*cis*-SUKSDORFIN AND RELATED PRODUCTS FROM JATAMANSINONE

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Abstract—The vasodilatory drug suksdorfin has been prepared from jatamanisinone and its stereochemistry established. Several interesting rearrangements observed during this investigation are recorded.

IN an earlier communication,[1]† jatamansinone (1; 3'-keto-3',4'-dihydroseselin) was used for the synthesis of the vasodilatory drugs dihydrosamidin(IV) and visnadin (V).[2,2a] For this purpose jatamansinone was converted to (±)-3'-keto-4'-acetoxy-3',4'-dihydroseselin (II) which was reduced with sodium borohydride to (±)-*cis*-4'-acetyl-khellactone (III) and the latter subsequently converted by treatment with appropriate acid chlorides to (±)-*cis*-dihydrosamidin and (±)-*cis*-visnadin.

In this paper we describe the conversion of the ketoacetate II to (±)-*cis*-suksdorfin (XIV).[4] Several interesting rearrangements were observed during this investigation.

As a prelude to the synthesis of suksdorfin, the ketoacetate II was saponified with aqueous alkali in an inert atmosphere, with a view to obtain 3'-keto-4'-hydroxy-3',4'-dihydroseselin (VI) but, instead a crystalline rearranged product, (compound A, $C_{14}H_{12}O_6$), showing an extended conjugation in its UV spectrum (λ_{max} 347, 312, 268 and 250 mμ; log ε 3·93, 4·09, 4·01 and 4·10 respectively) was obtained. The isovaleryl ester of this compound, m.p. 156–158°, does not show in the NMR spectrum any signal corresponding to proton attached to carbon bearing an ester group, and as it is resistant to sodium borohydride reduction, the presence of a tertiary OH group and the absence of a keto group in compound A may be assumed. The structure of this compound is being examined.

Alternatively, the ketoacetate II, was subjected to acid hydrolysis in dioxan solution, in an inert atmosphere. The crystalline, neutral product, thus obtained,

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† It appears that though the dark-brown variety of the plant[2a] material examined by us is true jatamansi, the greyish brown variety from which jatamansin was isolated is actually the umbelliferous plant *Selinum vaginatum*, C. B. Clarke, We are grateful to Prof. R. Hegnauer and Prof. K. E. Schulte for their interest and help in this identification.

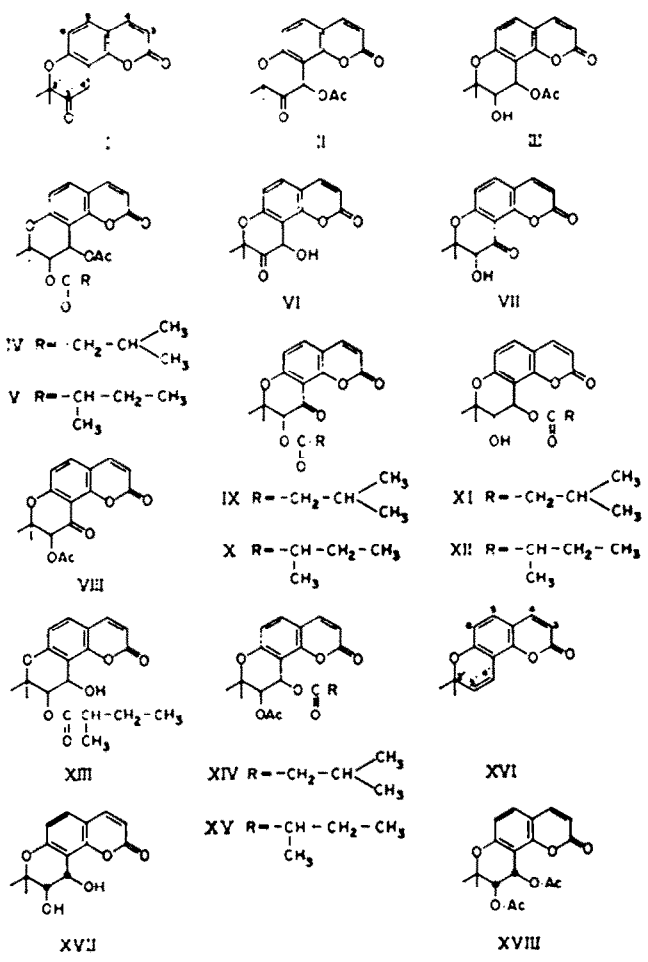
[1] S. N. Shanbhag, C. K. Mesta, M. L. Kaheshwari and S. C. Bhattacharyya, *Tetrahedron* **21**, 3591 (1965).

[2] E. Smith, N. Hosansky, W. G. Bywater and E. E. Van Tamelen, *J. Amer. Chem. Soc.* **79**, 3534 (1957).

[2a] H. D. Schroeder, W. Bencze, O. Halpern and H. Schmid. *Chem. Ber.* **92**, 2338 (1959). [3] S. D. Sastry, M. L. Maheshwari and S. C. Bhattacharyya, *Tetrahedron Letters* **10**, 1035 (1966).

[4] R. E. Willette and T. O. Soine, *J. Pharm. Sc.* **51**, 149 (1962).

CHART I.



m.p. 212–216°, shows the presence of extended conjugation in its UV spectrum (λ_{max} 348, 337, 308, 270, 242 and 217 mμ; log ε 3·92, 3·95, 3·97, 3·83, 3·86 and 4·22 respectively). Its NMR spectrum shows a singlet at much higher frequency (τ = 5·40, 1H) due to a proton attached to a carbon atom bearing a OH group, which indicates that the —CHOH group is not in the benzylic position. The NMR and UV spectra suggest that this compound is 3′-hydroxy-4′-keto-3′,4′-dihydroseselin (VII).

This was further confirmed by preparing its acetate derivative (VIII), which is different from the ketoacetate II. Evidently, during acid hydrolysis, the ketoalcohol VI rearranges to the ketoalcohol VII. Such rearrangements are well known.[4a]

As the sodium borohydride reduction product of the ketoacetate (VIII) is identical with (±)-*cis*-4′-acetyl-khellactone (III), obtained from sodium borohydride reduction of the ketoacetate II, the acyl group has migrated* from 3′ to 4′ position during

* We are grateful to Dr. J. L. Bose of our Laboratory for helpful discussion.

[4a] J. W. Baker, *Tautomerism* p. 285. London (1934).

reduction. Such types of acyl migrations are frequently observed in carbohydrate chemistry.[5]

(±) *cis* Suksdorfin (XIV), m.p. 134–136° was prepared by condensation of the ketoalcohol VII with isovaleryl chloride,[6] followed by the sodium borohydride reduction of (±)-3′-isovaleryloxy-4′-keto-3′,4′-dihydroseselin (IX) and subsequent acetylation of the resulting (±)-*cis*-4′-isovaleryl-khellactone (XI) formed via acyl migration. Its structure is fully supported by its NMR and UV spectra.

With a view to synthesize dihydropteryxin (XV), the ketoalcohol VII was condensed with α-methyl-butyryl chloride and the resulting (±)-3′-α-methylbutyryloxy 4′-keto-3′,4′-dihydroseslin (X) was reduced with sodium borohydride, (conditions similar to that used for other reductions) in order to obtain (±)-4′-α-methyl-butyryl-khellactone (XII). Instead the product was found to be (±)-3′-α-methyl-butyryl-khellactone (XIII), the structure of which was deduced from its NMR spectrum. Evidently there was no acyl migration during the sodium borohydride reduction of X. This was further proved by acetylation of XIII, which gave (±)-*cis*-visnadin (V), identical in all respects with that prepared earlier[1] by the condensation of (±)-*cis*-4′-acetyl-khellactone (III) with α-methyl-butyryl chloride. It has not therefore been possible for us to synthesize dihydropteryxin and the problem is receiving our further attention.

In order to prove the stereochemistry of dihydrosamidin, visnadin and suksdorfin, (±)-4′-acetyl-khellactone (III) was acetylated to (±)-3′,4′-diacetyl-khellactone (XVIII). This was found to be identical in all respects with authentic (±)-*cis*-3′,4′-diacetyl-khellactone obtained from seselin (XVI) through osmium tetroxide oxidation[3] followed by acetylation of the resulting (±)-*cis*-khellactone (XVII). This clearly indicates that both the acyloxy groups in the products mentioned above are *cis* oriented.

EXPERIMENTAL

All m.ps are uncorrected. Rotations were taken in chf soln. Silica gel used for column chromatography was activated by heating at 450° for 1 hr. Preparative TLC was done on silicic acid plates using benzene–AcOEt (1:1) as a developing solvent. The pet. ether refers to the fraction b.p. 60–80°. The help received from our microanalytical and spectroscopy sections is gretefully acknowledged.

Compound A. A suspension of the ketoacetate (2·05 g) in water (60 ml), containing KOH (3·30 g) was stirred under an atm of N, at the room temp for 4 hr. The reaction mixture was acidified with 4N H_2SO_4 (25 ml) and stirred at the room temp for an additional 45 min to ensure complete relactonization of the coumarin moiety. The product was extracted with ether, the ether extract washed with water, $NaHCO_3$aq and water, then dried (Na_2SO_4) and the solvent removed to give the residue (0·61 g) which was crystallized from benzene–acetone to give colourless crystals of compound A, m.p. 195–200°, UV spectrum: (described in the theoretical part). IR bands at: 3367, 2967, 2899, 1727, 1709, 1616, 1562, 1456, 1404, 1376, 1348, 1299, 1259, 1235, 1151, 1127, 1111, 1101, 1066, 1021, 917, 885, 847, 800 and 772 cm^{-1}. NMR spectrum (in pyridine); a doublet at τ = 3·67 (1H), J = 9 c/s; a pair of singlets at τ = 8·74 (3H) and 8·85 (3H, due to gem-dimethyl group). (Found: C, 65·00; H, 5·16 $C_{14}H_{12}O_5$ requires: C, 64·61; H, 4·65%.)

Isovaleryl ester of compound A. A suspension of the basic hydrolysis product (0·51 g) in dry benzene (80 ml) was added to isovaleryl chloride (300 mg) in dry benzene (10 ml). The mixture protected by a $CaCl_2$ guard tube, was refluxed on a steam bath under an atm of N for 50 hr. The course of reaction was followed by TLC on silicic acid. The reaction mixture was cooled, diluted with benzene, washed with $NaHCO_3$aq and then with water. The benzene soln was dried overnight (Na_2SO_4) and the solvent removed to afford a residue (0·065 g), which on chromatography over

[5] Ward Pigman, *The Carbohydrates* p. 147, Academic Press, N.Y. (1957).
[6] R. E. Willette and T. O. Soine, *J. Pharm. Sc.* 53, 275 (1964).

silicic acid (16 g) gave the isovaleryl ester of compound-A (0·6 g) in benzene–ether (93:7; 300 ml). This on crystallization from benzene–pet. ether gave colourless needles, m.p. 155–157°, $[\alpha]_D$ ±0°; UV spectrum λ_{max} 345, 308, 268 and 250 mμ (log ε 3·81, 4·03, 4·05 and 4·09 respectively); IR bands at: 2959, 1754, 1639, 1590, 1493, 1405, 1399, 1353, 1311, 1264, 1252, 1244, 1176, 1157, 1136, 1081, 1070, 1043, 969, 923, 891, 869, 853, 830, 787, 720, 686 cm^{-1}. NMR spectrum (in $CDCl_3$); a pair of doublets at τ = 2·28 (2H), J = 10 c/s; τ = 3·03 (1 H, J = 8 c/s; τ = 3·67 (1H), J = 9 c/s; singlets at τ = 7·78 (2H due to —$COCH_2$—group); τ = 8·78 (3H) and τ = 8·89 (3H due to *gem*-dimethyl group) and a doublet at τ = 9·04 (6H, J = 6 c/s, due to 1-Pr group). (Found: C, 66·03; H, 5·74; $C_{16}H_{20}O_6$ requires: C, 66·27; H, 5·85%.)

(±)-*3′-Hydroxy-4′-keto-3′,4′-dihydroseselin* (VII). HCl (2 ml conc acid + 6 ml water) was added to the soln of II (3·9 g) in dioxan (140 ml) and the mixture stirred at the room temp under an atm of N for 24 hrs. The dioxan was removed under reduced press and the product extracted with large excess of ether. The ether extract was washed with water, $NaHCO_3$aq and water, then dried (Na_2SO_4) and the solvent removed to give a residue (3·2 g) which on crystallization from benzene yielded pale yellow needles of VII, m.p. 212–216°; UV spectrum: (described earlier). IR bands at: 3448, 2941, 1748, 1704, 1613, 1562, 1497, 1471, 1437, 1381, 1361, 1258, 1242, 1227, 1176, 1143, 1124, 1111, 1079, 1010, 975, 930, 917, 854, 819, 800, 781, 771 and 724 cm^{-1}. NMR spectrum (in pyridine): a singlet at τ = 5·40 (1H, due to proton at 3′) and two singlets at τ = 8·33 (3H) and 8·65 (3H, due to *gem*-dimethyl group at 2′). (Found: C, 65·02; H, 4·85; $C_{14}H_{12}O_6$ requires: C, 64·61; H, 4·65%.)

(±)-*3′-Acetoxy-4′-keto-3′,4′-dihydroseselin* (VIII). Acetyl chloride (150 mg) was added to a soln of VII (101 mg) in benzene (30 ml) and kept at the room temp for 3 days. The course of reaction was followed by TLC on silicic acid. The reaction mixture was diluted with benzene (20 ml), washed with water, $NaHCO_3$aq and water, dried overnight (Na_2SO_4) and distilled. The residue (119 mg) was purified by preparative TLC on silicic acid and was crystallized from benzene to yield colourless needles of VIII m.p. 154–156°. UV spectrum: λ_{max} 348, 336, 305, 266 and 240 mμ (log ε 3·96, 3·98, 4·03, 3·96, 4·04 respectively). IR bands at: 2910, 1764, 1733, 1704, 1613, 1572, 1490, 1471, 1433, 1408, 1374, 1302, 1241, 1205, 1176, 1149, 1130, 1106, 1075, 925, 853, 837, 784, 769 and 743 cm^{-1}. NMR spectrum (in $CDCl_3$): doublets at τ = 2·35 (1H, J = 9 c/s, due to proton at 4;) τ = 2·56 (1H, J = 10 c/s, due to proton at 5); τ = 3·12 (1H, J = 9 c/s, due to proton at 6), τ = 3·69 (1H J = 9 c/s, due to proton at 3); singlets at τ = 4·45 (1H, due to proton at 3′); 7·76 (3H, due to

—C—CH_3 group); τ = 8·41 (3H) and τ = 8·60 (3H, due to *gem*-dimethyl group at 2′). (Found: C, 63·05; H, 5·26. $C_{16}H_{16}O_6$ requires: C, 63·15; H, 5·30%.)

(±)-*cis-4′-Acetyl-khellactone* (III). To a cooled (2–5°) stirred soln of VIII (94 mg) in dioxan (80%; 4 ml), a soln of $NaBH_4$ (18 mg) in dioxan aq. (1 ml) was added during a period of 5 min. The mixture was stirred for an additional 25 min at the same temp. The soln was made slightly acidic (pH 4–5) with 1N H_2SO_4, the solvent was removed under reduced press and the residue extracted with ether. The ether extract was washed with water, $NaHCO_3$aq and water, dried (Na_2SO_4) and evaporated to give residue (90 mg) from which III was isolated by preparative TLC on silicic acid. This was crystallized twice from benzene to give colourless crystals, m.p. 183–186°, which remained undepressed on admixture with an authentic specimen,[1] obtained by NaBHe reduction of II; IR, UV and NMR spectra of both the samples were identical. (Found: C, 62·86; H, 5·28. $C_{16}H_{18}O_6$ requires: C, 63·15; H, 5·30%.)

(±)-*3′-Isovaleryloxy-4′-keto-3′,4′-dihydroseselin* (IX). Ketoalcohol VII (0·66 g) was esterified with isovaleryl chloride (0·5 g) by following the procedure described earlier. The reaction product (0·84 g) was chromatographed on silica gel (22 g). Benzene–ether (95:5; 300 ml) eluted crude ester (0·750 g) which on crystallization from benzene–pet. ether afforded colourless needles of IX m.p. 122–124°. UV spectrum: λ_{max} 349, 337, 307, 268, 243, 218·5 mμ (log ε 3·99, 4·01, 4·05, 3·99, 4·06 and 4·12 respectively): IR bands at: 2941, 1754, 1718, 1608, 1575, 1471, 1439, 1385, 1351, 1304, 1285, 1250, 1215, 1190, 1176, 1136, 1124, 1110, 1078, 918, 850, 787 and 728 cm^{-1}. NMR spectrum (In $CDCl_3$): doublets at τ = 2·36 (1H, J = 9 c/s, due to proton at 4); τ = 2·42 (1H, J = 9 c/s, due to one proton at 5); τ = 3·13 (1H, J = 8 c/s, due to one proton at 6); τ = 3·69 (1H, J = 9 c/s, due to one proton at 3); singlets at τ = 4·43 (1H, due to one proton at 3′); τ = 7·67 (2H, due to —CO—CH_2 group); τ = 8·43 and τ = 8·63 (6H, due to *gem*-dimethyl group at 2′) and a doublet at τ = 8·96

(6H, J = 6 c/s, due to i-Pr group). (Found: C, 66·74; H, 5·90; $C_{19}H_{30}O_6$ requires: C, 66·27; H, 5·85%.)

(±)-*cis*-4′-*Isovaleryl-khellactone* (XI). Isovaleryl ester IX (0·273 g) was reduced with $NaBH_4$ (51 mg) by the procedure described earlier. The product (0·269 g) was subjected to preparative TLC on silicic acid plates from which (±)-*cis*-4′-*isovaleryl-khellactone* (0·196 g) was separated. This was crystallized from ether to give colourless crystals, m.p. 165–168°, UV spectrum: λ_{max} 326, 258, 248 and 214 mμ (log ε 4·11, 3·47, 3·50 and 4·08 respectively). IR bands at: 3472, 2950, 1745, 1721, 1626, 1504, 1475, 1418, 1379, 1295, 1269, 1250, 1225, 1192, 1168, 1153, 1133, 1117, 1693, 1072, 1020, 1012, 990 933, 900, 862, 848, 785, 775 and 767 cm^{-1}. NMR spectrum (in $CDCl_3$); doublets at τ = 2·36 (1H, J = 9 c/s, due to one proton at 4), τ = 2·66 (1H, J = 8 c/s, due to one proton at 5); τ = 3·17 (1H, J = 8c/s, due to one proton at 6); τ = 3·54 (1H, J = 5 c/s, due to one proton at 4′); τ = 3·74 (1H, J = 9 c/s, due to one proton at 3); τ = 5·94 (1H, J = 5 c/s, due to one proton at 3′); singlets at τ = 7·69 (2H, due to —CO—CH_3 group); τ = 8·55 (6H, due to *gem*-dimethyl group at 2′) and a doublet τ = 8·98 (6H, J = 6 c/s, due to i-Pr group). (Found: C, 65·55; H, 6·54. $C_{19}H_{28}O_6$ requires: C, 65·88; H, 6·40%.)

(±)-*cis-Suksdorfin* (XIV). Compound XI (0·105 g) was acetylated with acetyl chloride (0·150 g) by the procedure described earlier. The product (0·122 g) was purified by preparative TLC on silicic acid and was crystallized from EtOH–water and pet. ether to give colourless crystals, m.p. 134–136°. UV spectrum: λ_{max} 324, 299, 256, 245 and 213 mμ (log ε 4·10, 3·90, 3·52 3·58 and 4·13 respectively). IR bands at: 2941, 1754, 1623, 1506, 1475, 1410, 1379, 1362, 1297, 1233, 1163, 1119, 1099, 1076, 1027, 1005, 969, 956, 934, 909, 895, 896, 843, 826, 816 and 781 cm^{-1}. NMR spectrum (In $CDCl_3$): doublets at τ = 2·45 (1H, J = 9 c/s, due to one proton at 4); τ = 2·69 (1H, J = 8 c/s, due to one proton at 5), τ = 3·31 (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 = 3·86 (1H. J = 9 c/s, due to one proton at 3); τ = 4·77 (1H, J = 6 c/s, due to one proton at 3′); singlets at τ = 7·82 (2H, due to —$COCH_3$—group), τ = 7·93 (3H, due to —CO—CH_3 group): τ = 8·54 (6H, due to *gem*-diemthyl group at 2′); doublet at τ = 9·01 (6H, J = 6 c/s, due to i-Pr group). (Found: C, 64·78; H, 6·11. $C_{21}H_{24}O_7$ requires: C, 64·95; H, 6·23%.)

(±)-3′-α-*Methylbutyryloxy*-4′-*keto*-3′,4′-*dihydroseselin* (X). Ketoalcohol VII (0·82 g) was esterified with α-methylbutyryl chloride (0·61 g). The reaction product (1·01 g) was chromatographed on silica gel (26 g). Benzene–ether (95:5; 300 ml) eluted the crude ester (0·98 g) which on crystallization from benzene–pet. ether afforded colourless needles of X, m.p. 116–118; UV spectrum: λ_{max} 349, 337, 304, 266 and 240 mμ (log ε 3·98; 3·99, 4·04, 3·97 and 4·06 respectively). IR bands at: 2941, 1757, 1724, 1618, 1585, 1497, 1475, 1439, 1410, 1395, 1381, 1353, 1314, 1271, 1248, 1214, 1190, 1153, 1133, 1105, 1075, 1058, 1027, 1016, 978, 928, 906, 856, 830, 793, 784, 771, 751, 727 and 708 cm^{-1}. NMR spectrum (in $CDCl_3$); doublets at τ = 2·36 (1H, J = 10 c/s, due to one proton at 4); τ = 2·42 (1H, J = 9 c/s, due to one proton at 5); τ = 3·13 (1H, J = 8 c/s, due to one proton at 6); τ = 3·71 (1H, J = 9 c/s, due to one proton at 3); singlets at τ = 4·44 (1H, due to one proton at 3′), τ = 8·44 and τ = 8·62 (3H, each, due to *gem*-dimethyl group at 2′), a doublet at τ = 8·75 (3H, J = 7 c/s, due to CH_3—CH< grouping) and a triplet at τ = 9·02 (3H, due to CH_3—CH_2— grouping). (Found: C, 66·28; H, 5·78. $C_{19}H_{20}O_6$ requires: C, 66·27; H, 6·85%.)

(±)-*cis*-3′-α-*Methylbutyryl-khellactone* (XIII). Compound X (0·44 g) was reduced with $NaBH_4$ (84 mg). The product (0·43 g) was chromatographed on silicic acid (12 g). Benzene–ether (75:25; 250 ml) eluted the crude alcohol, which was crystallized from benzene to give colourless needles of XIII, m.p. 176–178°. UV spectrum: λ_{max} 324, 258, 256, 219·5 and 213·5 mμ (log ε 4·09, 3·47, 3·50, 4·06 and 4·09 respectively). IR bands at: 3546, 2959, 2907, 1730, 1629, 1511, 1475, 1416, 1389, 1379, 1344, 1294, 1279, 1247, 1193, 1170, 1157, 1133, 1119, 1079, 1062, 1020, 1012, 980, 936, 893, 847, 781 769 and 756 cm^{-1}. NMR spectrum (in $CDCl_3$): doublets at τ = 2·35 (1H, J = 10 c/s, due to proton at 4); τ = 2·68 (1H, J = 8 c/s, due to proton at 5); τ = 3·23 (1H, J = 9 c/s, due to proton at 6); τ = 3·79 (1H, J = 9 c/s, due to proton at 3); τ = 4·78 and 5·02 (1H each, J = 5 c/s, due to protons at 3′ and 4′); singlets at τ = 8·5 and 8·6 (6H, due to *gem*-dimethyl group at 2′); a doublet at τ = 8·87 (3H, due to CH_3—CH< grouping and a triplet at τ = 9·15 (3H, due to CH_3—CH_2— grouping). (Found: C, 65·98; H, 6·52. $C_{19}H_{22}O_6$ requires: C, 65·88; H, 6·40%.)

(±)-*cis-Visnadin* (V). Compound XIII (0·16 g) was acetylated with acetyl chloride (0·20 g). The product was chromatographed on silica gel (6 g). Benzene–ether mixture (95:5; 150 ml) eluted

the crude product (0·18 g) which was crystallized from EtOH–water and pet. ether to give colourless needles of V, m.p. and mixed m.p. with (±)-*cis*-visnadin, prepared earlier, 151–153°. IR, UV and NMR spectra of both the samples were identical. (Found: C, 65·05; H, 6·40. $C_{21}H_{24}O_7$ requires: C, 64·95; H, 6·23%.)

(±)-*cis-Khellactone*[7,8] (XVII). Osmium tetroxide (0·41 g) in dry purified dioxan (5 ml) was added to seselin (0·29 g) in the same solvent (5 ml). The soln was left at the room temp for 4 days and then saturated with H_2S. The black ppt was filtered off and the dioxan soln was evaporated to dryness under reduced press. The crude product (0·31 g) was crystallized from benzene to give colourless crystals of XVII, m.p. 159–161°. UV spectrum: λ_{max} 325, 258, 246, 219·5 and 213 mμ (log ε 4·14, 3·45, 3·48, 4·10 and 4·13 respectively). IR bands at: 3390, 2899, 1728, 1696, 1616, 1492, 1398. 1369, 1352, 1289, 1242, 1225, 1180, 1160, 1138, 1114, 1091, 1050, 1021, 1006, 999, 930, 890, 855, 822, 802, 780, and 752 cm^{-1} (Found: C, 64·03; H, 5·53, $C_{14}H_{14}O_5$ requires: C, 64·11; H, 5·38%.)

(±)-*cis*-3′,4′-*Diacetyl-khellactone* (XVIII) *from* (±)-*cis-khellactone*[8] (XVII). (±)-*cis*-khellactone (0·906 g) was acetylated with acetyl chloride (0·40 g). The reaction product (0·11 g) was purified by preparative TLC and then crystallized from pet. ether–benzene to give colourless needles of XVIII m.p. 160–162°. UV spectrum: λ_{max} 322, 296, 256, 245 and 219·5 mμ (log ε 4·14, 3·94, 3·53, 3·60 and 4·15 respectively). IR bands at: 2941, 2899, 1764, 1742, 1631, 1508, 1477, 1412, 1389, 1312, 1287, 1245, 1195, 1163, 1136, 1087, 1063, 1031, 1018, 994, 952, 923, 899, 856, 843, 823, 800, 781 and 759 cm^{-1}. (Found: C, 62·52; H, 5·32. $C_{18}H_{18}O_7$ requires: C, 62·42; H, 5·24%.)

(±)-*cis*-3′,4′-*Diacetyl-khellactone* (XVIII) *from* (±)-*cis*-4′-*acetyl-khellactone* (III). (±)-*cis*-4′-Acetyl khellacetone (0·085 g) was acetylated with acetyl chloride (0·3 g). The product (0·092 g) after purification by preparative TLC and crystallization from pet. ether–benzene gave colourless needles of XVIII, m.p. and mixed m.p. with the sample prepared as above, 159–161°. IR and UV spectra of both preparation are completely superimposible. (Found: C, 62·38; H, 5·18. $C_{18}H_{18}O_7$ requires: C, 62·42; H, 5·24%.)

[7] D. H. R. Barton and Dov. Elad, *J. Chem. Soc.* 2085 (1956).