VIa is insoluble in water, sparingly soluble in ethanol, and soluble in hot glacial acetic acid; it gives a red color with concd. sulfuric acid.

One gram of IXa[7] was dissolved in hot 20% aqueous sodium hydroxide solution, and the solution was immediately cooled and acidified with dilute sulfuric acid. The crystals so obtained (*ca.* 900 mg.), m.p. 275–279°, were identified as VIa (melting point and mixed melting point).

(*b*) IVb. Similarly, treatment of IVb with ammoniacal silver nitrate solution under the above conditions led to VIb, which crystallized as pale yellow needles from glacial acetic acid, m.p. 256°.

Anal. Calcd. for $C_{13}H_8O_6$: C, 60.00; H, 3.40. Found: C, 59.92; H, 3.44.

VIb is insoluble in water, very sparingly soluble in benzene, and freely soluble in hot glacial acetic acid. It reacts with sodium bicarbonate solution with the separation of a sparingly soluble crystalline sodium salt. Crystals of VIb turn red when treated with concentrated sulfuric acid.

Synthesis of VIb. *Ethyl 4-methoxy-6-hydroxycoumarone-5-α,γ-diketobutyrate* (VIIIb). It was obtained after the procedure of Schönberg and Sina by the condensation of visnaginone (VIIb) with diethyl oxalate in the presence of sodium; colorless needles from ethanol, m.p. 95° (red melt); yield, *ca.* 25%.

Anal. Calcd. for $C_{15}H_{14}O_7$: C, 58.82; H, 4.57. Found: C, 58.67; H, 4.83.

VIIIb gives a reddish-brown color with ferric chloride and dissolves in aqueous sodium hydroxide solution (4%) with a yellow color.

2-Carboxyethyl-5-methoxyfuro-4′,5′,6,7-chromone (IXb). A solution of 1 g. of VIIIb in hot 20 ml. of ethanol was treated with 0.5 ml. of sulfuric acid and 10 ml. of ethanol. The reaction mixture was kept for 24 hr. at room temperature (25°). The yellow crystals (0.80 g.) melted at 167–168°.

Anal. Calcd. for $C_{15}H_{12}O_6$: C, 62.50; H, 4.16. Found: C, 62.38; H, 4.26.

IXb is sparingly soluble in water, insoluble in aqueous sodium hydroxide solution (4%), and soluble in benzene, chloroform, and glacial acetic acid. It gives a deep red color with sulfuric acid.

5-Methoxyfuro-4′,5′,6,7-chromone-2-carboxylic acid (VIb). When a mixture of 0.5 g. of IXb and 2.5 ml. of aqueous sodium hydroxide (4%) was gently heated (water bath, 65°), the solid went into solution in a few minutes. The solution was immediately diluted with water, and acidified with dilute sulfuric acid to give 0.4 g. of yellow crystals, m.p. 252–254°, identified as VIb (melting point and mixed melting point with a specimen prepared as above).

Action of aluminum isopropoxide on: (*a*) *khellin* (Ia). To a solution of 3.2 g. of Ia in 20 ml. of hot isopropyl alcohol was added a solution of aluminum isopropoxide (prepared from 1 g. of aluminum foil, 50 mg. of mercuric chloride, 20 ml. of isopropyl alcohol, and 0.2 ml. of carbon tetrachloride). The reaction mixture was refluxed for 2 hr. and was then distilled to half its volume. It was poured into 400 ml. of iced dilute hydrochloric acid, and the copious yellow precipitate thus obtained was collected and crystallized from ethanol to give 2 g. of 5-norkhellin (XIa), m.p. 197–200° (not depressed by admixture with an authentic specimen of XIa prepared by demethylation of Ia with hydrochloric acid or hydrobromic acid.[8a]

(*b*) *Visnagin* (Ib). 5-Norvisnagin (XIb) was obtained, upon treatment of Ib with aluminum isopropoxide as described above, m.p. 154–156° (not depressed by admixture with an authentic specimen of XIb, prepared by demethylation of Ib with hydrochloric acid.[14]

Acknowledgment. The authors are indebted to Professor Alexander Schönberg for his interest during this investigation.

CAIRO, EGYPT, U.A.R.

(14) A. Schönberg and N. Badran, *J. Am. Chem. Soc.*, **73**, 2960 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, CAIRO UNIVERSITY, AND THE LABORATORIES OF THE MEMPHIS CHEMICAL CO.]

Experiments with Chromeno-α-pyrone. Reactions of Provismine (Visnadin)

AHMED MUSTAFA, NICOLAS A. STARKOVSKY, AND TAYSEER I. SALAMA

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3′-Keto-3′,4′-dihydroseselin (II) now has been obtained in 40% yield by the controlled hydrolysis of provismine (visnadin) (I) with alcoholic sulfuric acid. Mild treatment of I with the same reagent led to the formation of khellactone (IV) which can be smoothly converted to II by heating with 10*N* sulfuric acid.

II reacts readily with common ketonic group reagents to give the corresponding derivatives (VIa–d), and reacts in the enolic form with acetic anhydride to form 3′-acetoxyseselin (V). It undergoes condensation reactions with the 4′-methylene group to give the condensation products VIe–g and VII.

Reduction of II with aluminum isopropoxide gives 3′-hydroxy-3′,4′-dihydroseselin (IXa), which is readily converted to seselin (X) upon sublimation with phosphorus pentoxide.

Ammi visnaga L., a plant indigenous to the Mediterranean regions, has been used in Egypt for centuries as a home remedy and spasmolytic.[1]

That the seeds contain biologically active substances other than the chromones, khellin, visnagin, and khellol glucoside[2] has been shown by Samaan,[3] whose "visnagan" fraction (the oil remaining after removal of all crystalline material) evidenced considerable vasodilatory activity. Visnagan was subsequently investigated by Cavallito and Rockwell,[4] Smith, Pucci, and Bywater,[5a] and later, by

(1) For a complete review on the subject, *cf.* H. Schmid, *Fortschritte der chemie organische Naturstoffe*, Vienna, L. Zechmeister (Ed.), **11**, 124 (1954).

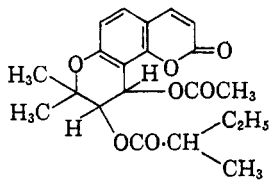
(2) E. Späth and W. Gruber, *Ber.*, **71**, 106 (1938); **74**, 1549 (1941).

(3) K. Samaan, *Quart. J. Pharm. Pharmacol.*, **4**, 14 (1931); **6**, 12 (1933); **18**, 83 (1945).

(4) C. J. Cavallito and H. E. Rockwell, *J. Org. Chem.*, **15**, 820 (1950).

(5) (a) E. Smith, L. A. Pucci, and W. G. Bywater, *Science*, **115**, 520 (1952); (b) E. Smith, N. Hosansky, W. G. Bywater, and E. E. van Tamelen, *J. Am. Chem. Soc.*, **79**, 3534 (1957).

Smith, Hosansky, Bywater, and van Tamelen,[5b] who identified the three potent vasodilatory natural coumarins, namely, samidin, dihydrosamidin, and visnadin. The latter substance has been obtained in 0.08% yield after the procedure described by Smith, *et al.*[5b] A systematic study of the chemical constituents of the different parts of the plant, other than the seeds, now has shown that the umbels of the plant are particularly rich in natural coumarins; working up their petroleum ether extract led to the isolation of a crystalline product, called provismine,[6] in 0.35% yield.[7] Provismine (I) now has proved to be identical with visnadin (molecular formula $C_{21}H_{24}O_7$; colorless needles from hexane; m.p. 83–86, $[\alpha]_D^{20}$ + 9.25° (alc.) and m.p. 84–86° or 85–88°, $[\alpha]_D^{20}$ + 9°(alc.)[5b] respectively).



I

Moreover, paper chromatography study (*cf.* Table I) has revealed the comparatively high purity of the crude umbel extract as provismine (visnadin), together with a small amount of visnagin and traces of khellin could be easily detected. An impurity, giving a separate blue spot with R_f = 0.31 similar to that given by provismine (visible after spraying with sodium hydroxide and drying), was occasionally noted, otherwise, pure I was easily obtained by simple repeated crystallization.

TABLE I

Substance	Color of Spot under Ultraviolet Light: Before spraying with 4% aq. NaOH	Color of Spot under Ultraviolet Light: After Spraying with 4% NaOH and drying to 80°	R_f (T = 20° ± 3) Ascending Method Developing Solvent: Water
Provismine	No color	Blue	0.18
Visnagin	Intense blue	Violet	0.32
Khellin	Yellow-green	Yellow-gray	0.42
Khellol glucoside	Pale gray	Pale blue-gray	0.53

The aim of the present investigation is to prepare a number of derivatives of provismine, retaining the dihydroseselin structure, with the view of obtaining pharmacologically active water-soluble derivatives.[8]

3′-Keto-3′,4′-dihydroseselin (II) now has been easily prepared by the controlled hydrolysis of provismine (I) with alcoholic sulfuric acid, the yield being 40%. The yields of II, prepared by different authors,[5b,9,10] principally based on the preliminary conversion of I to methylkhellactone (III), followed by demethylation of the latter compound to the diol, namely, khellactone (IV), which is then dehydrated to II, do not exceed 20%, though it is possible to carry out the last two steps simultaneously. Mild treatment of I with alcoholic sulfuric acid led to the formation of IV ($[\alpha]_D^{24}$ + 12.5°) apparently identical with the diol IV obtained by Smith, *et al.*[5b] from samidin *via* the corresponding methylkhellactone. Heating of III with aqueous 10*N* sulfuric acid brought easily its conversion to II. This, coupled with the fact that II readily crystallizes, and the fact that II possesses the highly reactive —CH_2—C(=O)— system and a potential ketol group (>C(OH)—C(=O)—CH_2—) prompted us to the choice of II as an intermediate for the preparation of the new derivatives described in this paper.

The ketone II displays a keto-enol tautomerism, is soluble in dilute sodium hydroxide solution, and yields both an acetyl derivative, *viz.*, 3′-acetoxyseselin (V) and an oxime (VId). It reacts with the common ketone reagents to give the corresponding hydrazone (VIa), semicarbazone (VIb) and thiosemicarbazone (VIc) derivatives. The presence of an active methylene group attached to C-4′ is indicated by its ready condensation with nitrous acid, *p*-nitrosodimethylaniline, and diazotized aniline to give the corresponding 4′-oximino-(VIe), *p*-dimethylaminophenylazomethine-(VIf), and azophenyl derivatives (VIg), respectively.

We have been unable to bring II to undergo the Mannich reaction to get the corresponding amino derivatives, a fact which prompted us to study the behavior of II toward the action of formaldehyde. Thus, when an alcoholic (methyl or ethyl alcohol) solution of II was treated with an excess of 35% formaldehyde solution, the corresponding 4′-methylene derivative (VIh) was obtained. On the other hand, refluxing an alcoholic solution of II with an equivalent amount of paraformaldehyde and one drop of hydrochloric acid, effected the formation of a colorless product for which structure VII is proposed, not beyond complete doubt. The latter compound has also been isolated when II was allowed to undergo the Mannich base reaction in the presence of a primary or a secondary amine and the calculated amount of paraformaldehyde.

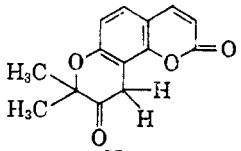
(6) N. Badran and N. A. Starkowsky, *Proc. Pharm. Soc. Egypt, Sci. Ed.*, **38**, 93 (1956).

(7) H. Abu-Shady, *Proc. Pharm. Soc. Egypt, Sci. Ed.*, **38**, 99 (1956).

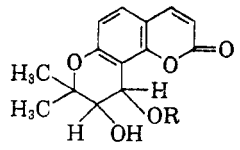
(8) Provismine is highly insoluble in water.

(9) E. Späth, W. Gruber, and O. Matzke, *Canadian J. Chem.*, **31**, 715 (1953).

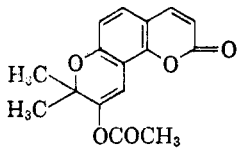
(10) W. Bencze and H. Schmid, *Experientia*, **10**, 12 (1954); W. Bencze, O. Halpern, and H. Schmid, *Experientia*, **12**, 137 (1956).



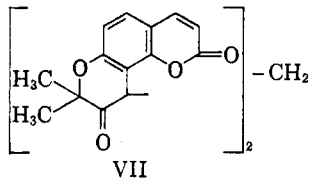
II



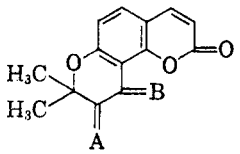
III. R = CH_3
IV. R = H



V



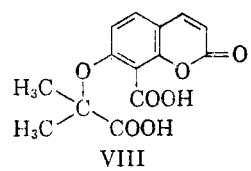
VII



VI

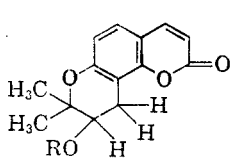
a. A = NNH_2; B = H_2
b. A = $NCONHNH_2$; B = H_2
c. A = $NCSNHNH_2$; B = H_2
d. A = NOH; B = H_2
e. A = O; B = NOH
f. A = O; B = p-$NC_6H_4N(CH_3)_2$
g. A = O; B = N—NHC_6H_5
h. A = O; B = CH_2
i. A = B = O

Treatment of II with selenium dioxide effected the oxidation of the methylene group to a carbonyl group with the formation of 3′,4′-diketo-3′,4′-dihydroseselin (VIi) which has also been obtained by acid hydrolysis of VIf. VIi afforded a quinoxaline derivative by condensation with *o*-phenylenediamine. On the other hand, oxidation of II with hydrogen peroxide in alkaline medium led to a carboxylic acid believed to have a structure like VIII as the analysis corresponds to the molecular formula $C_{14}H_{12}O_7$.

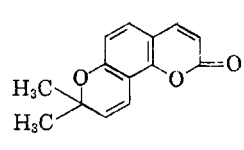


VIII

Reduction of II with aluminum isopropoxide gave 3′-hydroxy-3′,4′-dihydroseselin (IXa), which, upon dehydrative sublimation with phosphorus pentoxide, was converted to seselin (X).



IX



X (Seselin)

a. R = H
b. R = $COCH_3$

EXPERIMENTAL[11]

The provismine (I), used in this investigation, was prepared after Abu-Shady,[7] and purified by successive recrystallizations from petroleum ether (b.p. 60–80°) until no yellow color was developed when its chloroform solution was shaken with 10*N* sulfuric acid. It melted at 83–86°.

3′-Keto-3′,4′-dihydroseselin (II). To 4 g. of I was added a mixture of 8 ml. of sulfuric acid and 72 ml. of ethanol; the reaction mixture was refluxed (water bath) for 3 hr. It was then slowly distilled to one-third of its volume, submitted to steam distillation (500 ml. collected distillate), and the remaining mixture was further concentrated to about 50 ml. The semisolid, that separated upon cooling, was collected, washed with water, and crystallized from alcohol (charcoal) as colorless crystals (*ca.* 1.5 g.), m.p. 157–158°, (reported[5b] m.p. 156–157°).

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95; active hydrogen, 0.41. Found: C, 68.78; H, 4.72; active hydrogen, 0.50.

II is insoluble in water, sparingly soluble in ethanol. It gives a deep orange color with potassium hydroxide pellets moistened with alcohol, and reduces Fehling's solution and ammoniacal silver nitrate solution.

The above experiment was repeated, but the reaction mixture after dilution with an equal volume of water, was steam distilled (500 ml., collected distillate) until 150 ml. remained in the distilling flask. It was filtered while hot, cooled, and the solid, so obtained, was crystallized from water as colorless needles (*ca.* 1 g.), m.p. 185–186°, $[\alpha]_D^{24}$ +12.5 (*c*, 1.0 alc.) (reported m.p. 180–182°, $[\alpha]_D$ +13 (*c*, 0.7 alc.,); identified as 3′,4′-dihydroxy-3′,4′-dihydroseselin (khellactone) (IV).

Anal. Calcd. for $C_{14}H_{14}O_5$: C, 64.11; H, 5.38; active hydrogen, 0.77. Found: C, 63.92; H, 5.30; active hydrogen, 0.76.

IV is readily soluble in alcohol and boiling water (1:60). It is insoluble in aqueous sodium hydroxide solution, and does not reduce Fehling's solution, but readily reduces Tollen's reagent.

When 0.5 g. of IV was heated (water bath) with 30 ml. of 50% sulfuric acid for 1 hr., followed by dilution with water and cooling, 350 mg. of II was obtained.

The hydrazone of II. VIa was obtained, in an almost quantitative yield, when a mixture of a solution of 1 g. of II in 20 ml. of hot ethanol and 0.4 ml. of hydrazine hydrate was heated to boiling and kept aside to cool. It gave colorless prisms from alcohol, m.p. 209–211°.

Anal. Calcd. for $C_{14}H_{14}N_2O_3$: C, 65.10; H, 5.46; N, 10.85. Found: C, 65.22; H, 5.48; N, 11.20.

The semicarbazone of II. To a solution of 488 mg. of II in 15 ml. of hot ethanol was added a solution of 245 mg. of semicarbazide hydrochloride in 5 ml. of 5% hydrochloric acid. The reaction mixture was allowed to stand overnight at room temperature, and the colorless crystals of VIb (320 mg.), that separated, melted at 247° dec.

Anal. Calcd. for $C_{15}H_{15}N_3O_4$: C, 59.79; H, 5.01; N, 13.94. Found: C, 59.98; H, 5.20; N, 14.00.

The thiosemicarbazone of II. Similarly, VIc was obtained as colorless crystals from alcohol, m.p. 221° dec.

Anal. Calcd. for $C_{15}H_{15}N_3SO_3$: C, 56.76; H, 4.76; N, 13.24; S, 10.10. Found: C, 56.70; H, 4.67; N, 13.55; S, 10.50.

The oxime of II. A mixture of 0.8 g. of hydroxylamine hydrochloride, 1.2 g. of fused sodium acetate, 1 g. of II, and 60 ml. of ethanol was refluxed (water bath) for 1.5 hr. The reaction mixture was poured into ice water and the solid, so obtained, was crystallized from alcohol to give colorless prisms (*ca.* 0.5 g.) of VId, m.p. 224–225°. It is soluble in hot alcohol, but is difficultly soluble in water.

Anal. Calcd. for $C_{14}H_{13}NO_4$: C, 64.85; H, 5.05; N, 5.40. Found: C, 64.86; H, 5.06; N, 5.41.

(11) All melting points are uncorrected. Elementary microanalyses were made by Drs. Weiler and Strauss, Oxford.

3'-Acetoxyseselin (V). Refluxing a solution of 1 g. of II in 5 ml. of acetic anhydride in the presence of 1 g. of freshly fused sodium acetate for 1 hr., followed by pouring the cooled reaction mixture into ice water gave colorless crystals of V which, upon recrystallization from 50% ethanol, melted at 115°; yield, almost quantitative.

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.12; H, 4.92; —$COCH_3$, 15.04. Found: C, 67.02; H, 4.83; —$COCH_3$, 15.5.

V is difficultly soluble in water, but is soluble in alcohol; it does not dissolve in 4% aqueous sodium hydroxide solution.

3'-Keto-4'-oximino-3',4'-dihydroseselin (VIe). To a cooled solution of 2 g. of II in 100 ml. of ethanol was added 8 ml. of hydrochloric acid and a solution of 4 g. of sodium nitrite in 16 ml. of water. The reaction mixture was kept aside overnight, and the solid (*ca.* 2 g.), so obtained, was collected and washed thoroughly with water. It crystallized from ethanol as colorless crystals, m.p. 223–224° dec.

Anal. Calcd. for $C_{14}H_{11}NO_5$: C, 61.53; H, 4.05; N, 5.12. Found: C, 61.48; H, 4.26; N, 4.67.

VIe dissolves in 4% aqueous sodium hydroxide solution with a yellow color, and gives a brown-red color with ferric chloride (turning yellow on warming and reverting to brown-red on cooling).

4'-(p-Dimethylaminophenylazomethine)-3'-keto-3',4'-dihydroseselin (VIf). Dark green crystals of VIf (*ca.* 800 mg.) were obtained, upon adding to a solution of 1.22 g. of II in boiling ethanol a solution of 0.75 g. of *p*-nitrosodimethylaniline in 15 ml. of the same hot solvent; m.p. 206° dec. VIf is insoluble in water, but is soluble in chloroform giving a violet solution.

Anal. Calcd. for $C_{22}H_{20}N_2O_4$: C, 70.19; H, 5.35; N, 7.44. Found: C, 69.99; H, 5.25; N, 7.25.

4'-Azophenyl-3'-keto-3',4'-dihydroseselin (VIg). To a cold diazotized solution of 120 mg. of aniline hydrochloride was added a cold solution of 200 mg. of II in 20 ml. of ethanol. The reaction mixture was then kept aside overnight at room temperature, and the collected colored precipitate was crystallized from ethanol as orange needles, m.p. 205–206° (red melt); yield *ca.* 180 mg.

Anal. Calcd. for $C_{20}H_{16}N_2O_4$: C, 68.95; H, 4.63; N, 8.04. Found: C, 69.15; H, 4.81; N, 7.85.

VIg is insoluble in water, and does not dissolve in 4% aqueous sodium hydroxide solution. Its crystals turned deep violet upon treatment with sulfuric acid and gradually dissolved to give a deep red solution.

3'-Keto-4'-methylene-3',4'-dihydroseselin (VIh). Refluxing a solution of 550 mg. of II in 10 ml. of hot ethanol with 2 ml. of formaldehyde solution (35%) for 1 hr., gave upon cooling 350 mg. of colorless crystals of VIh which melted, after recrystallization from ethanol at 213–214°.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.34; H, 4.99.

4,4'-Methylenebis(3'-keto-3',4'-dihydroseselin) (VII). A mixture of 0.5 g. of II, 66 mg. of paraformaldehyde, 1 drop of concd. hydrochloric acid, and 20 ml. of methanol was refluxed for 3 hr. Upon cooling, 340 mg. of colorless crystals of VII were collected and recrystallized from ethanol, m.p. 173–175°. VII was similarly obtained when ethanol was used for methanol in the reaction mixture, or when the reaction was carried out in the presence of 1 equivalent of methylamine or dimethylamine hydrochloride. It is insoluble in water and in 4% aqueous sodium hydroxide solution.

Anal. Calcd. for $C_{29}H_{24}O_8$: C, 69.59; H, 4.83. Found: C, 69.66; H, 4.53.

7-(β-Carboxyisopropyloxy)-8-carboxycoumarin (VIII). To a mixture of 1 g. of II and 50 ml. of ice cooled aqueous sodium hydroxide solution (5%) was added dropwise 4 ml. of hydrogen peroxide (30%). The temperature of the reaction mixture was kept below 5°. It was then allowed to stand at room temperature for 2 hr., and was acidified with 25% sulfuric acid. The turbid reaction mixture was extracted with chloroform, and the aqueous layer was saturated with common salt and kept in the refrigerator overnight. The colorless crystals (*ca.* 520 mg.) of VIII that separated were recrystallized from hot water, m.p. 258° dec.

Anal. Calcd. for $C_{14}H_{12}O_7 \cdot 2H_2O$: C, 51.22; H, 4.90. Found: C, 51.30; H, 4.80.

VIII is soluble in hot water and alcohol, but is almost insoluble in chloroform. It dissolves in aqueous sodium bicarbonate solution with effervescence and its aqueous solution gives a buff precipitate with aqueous ferric chloride solution.

3'-Hydroxy-3',4'-dihydroseselin (IXa). A solution of II (0.5 g.) in 25 ml. of isopropyl alcohol was treated with 3 ml. of a solution of aluminum isopropoxide (3 equivalents) in the same solvent. The reaction mixture was slowly distilled until no more acetone was collected; it was then decomposed with ice cold dilute sulfuric acid, and the solid which separated was crystallized from dilute ethanol and water as colorless needles, m.p. 165.5–167°; yield, *ca.* 0.2 g.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.04; H, 5.71.

Treatment of 0.5 g. of IXa with acetic anhydride and sodium acetate, as described for V, gave 0.3 g. of colorless plates (from ethanol) of 3'-acetoxy-3',4'-dihydroseselin (IXb), m.p. 175°.

Anal. Calcd. for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.59; H, 5.66.

When a mixture of 100 mg. of IXa and 200 mg. of phosphorus pentoxide was sublimed under reduced pressure (10 mm.) at 120–150° (bath temp.), seselin (X) was obtained, which upon recrystallization from dilute alcohol gave colorless needles, m.p. 120°[12]; yield *ca.* 50 mg.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.29. Found: C, 73.03; H, 4.69.

3',4'-Diketo-3',4'-dihydroseselin (VIi). (a) VIf (700 mg.) was shaken in a separating funnel with 40 ml. of chloroform and 40 ml. of 50% sulfuric acid. The deep violet chloroform layer, which was decolorized in a few minutes was separated from the yellow acid layer, washed with water, dried, and distilled to dryness. The yellow solid residue thus obtained was crystallized twice from hot water to give yellow needles of VIi, m.p. 254–256°; yield, *ca.* 150 mg.

Anal. Calcd. for $C_{14}H_{10}O_5 \cdot H_2O$: C, 60.87; H, 4.37. Found: C, 61.19; H, 4.60.

VIi is easily soluble in alcohol, chloroform and boiling water. Crystals of VIi turn deep yellowish-brown upon treatment with sulfuric acid, and give a yellow solution with alcoholic potassium hydroxide solution.

(b) VIi was obtained directly from II when a solution of 1 g. of the latter in 30 ml. of *n*-butyl alcohol was refluxed with 0.6 g. of selenium dioxide for 24 hr. After filtration and evaporation of the solvent under reduced pressure, the solid residue was crystallized from water to give 600 mg. of VIi, m.p. 252–256°, not depressed by an authentic specimen obtained as above.

VIi, upon treatment with excess of 2,4-dinitrophenylhydrazine in the conventional manner, gave an orange mono-2,4-dinitrophenylhydrazone derivative, which, after recrystallization from acetic acid, melted at 322–324°.

Anal. Calcd. for $C_{20}H_{14}N_4O_8$: N, 12.76. Found: N, 12.30.

Preparation of the quinoxaline of VIi. A solution of 0.258 g. of VIi and 0.108 g. of *o*-phenylenediamine in 25 ml. of glacial acetic acid was refluxed for 1 hr. The solution was then poured into ice cold water and the precipitate of the quinoxaline derivative was crystallized from ethanol to give pale yellow needles, m.p. 190–191°; yield *ca.* 0.2 g.

Anal. Calcd. for $C_{20}H_{14}N_2O_3$: C, 72.72; H, 4.27; N, 8.48. Found: C, 72.73; H, 4.58; N, 8.26.

The quinoxaline derivative gave an intense red-black color with concentrated sulfuric acid and dissolved in alcoholic sodium hydroxide solution with a deep yellow color.

CAIRO (EGYPT), U.A.R.

(12) P. K. Bose and N. C. Guha, *Sci. and Cult.*, **2**, 236 (1936) reported m.p. 120° for X.