1,3-cyclohexadiene **4**, still as the *syn*-oxime, by the NMR spectrum ($CDCl_3$). The isopropenyl signals of **1** were absent, the CH=N singlet was only slightly downfield (δ 7.77) from that in **1**, the olefinic protons formed an AB quartet (doublets at δ 6.09 and 5.78, J = 6.0 Hz), and a 6-proton doublet characteristic for isopropyl methyls was at δ 1.03 (J = 6.7 Hz); the difference $^{\delta}OH-{}^{\delta}CH$ in dimethylsulfoxide-d_6 was 3.00 ppm. UV-absorption of **4** was at 304 nm (ε 19,100) in ethanol[9]. If the BF_3 treatment was halted after 20 min, an NMR spectrum showed that **1** was already completely transformed, and that a 40:60 mixture of **4** with the 1,4-cyclohexadiene *syn*-oxime **5** was obtained.

Under the conditions tried so far, only one oxime (**1**) can be obtained from perillartine. Probably the true *anti* form (**2**) does not exist under normal circumstances. On the basis of this and other work in progress[10], it seems to be a generality that *α,β-unsaturated aldoximes bearing an alkyl substituent on the α-carbon exist only in the* syn *form. Anti* forms should then be expected only under extraordinary conditions, or as a result of exceptional structural features which may favor the *anti* form in certain molecules. It must be emphasized that the case with aromatic, as opposed to olefinic, unsaturation in the α,β-position is quite different. Benzaldehydes commonly form both oximes, and the occurrence of **4** in only the *syn* form is in contrast to the easy isolation of both *syn* and *anti* oximes from *p*-isopropylbenzaldehyde[10].

When examined as the dry solid, the chloride **3** was tasteless, as was reported[1] when this compound was thought to be the β-oxime from **1**. It could not be studied in solution, even at a very low concentration, as on exposure for 2 h to water, **3** partially decomposed with elimination of hydrogen chloride. In comparison, perillartine as the dry solid was about twice as sweet as solid sucrose, but was less sweet than cyclamate or saccharin (which, as solids, were judged[10] to be 5 times and 7 times as sweet as sucrose, respectively). The 1,3-diene **4** had as the solid a sharp, peppery taste. The flavor qualities of **1** and **4** were also imparted to water in contact with the solids, even though the actual solubilities were extremely low. These properties are being studied further.

Riassunto. Viene confermato che la struttura dell'agente dolcificante perillartina è quella di una *sim* ossima. Il tentativo di ottenere l'isomero *anti* per azione dell'acido cloridrico ha condotto invece all'addotto tra HCl e gruppo isopropenilico, mentre il trattamento con trifluoruro di boro ha provocato solo la migrazione del doppio legame per formare l'analogo derivato dell'1,3-cicloesadiene.

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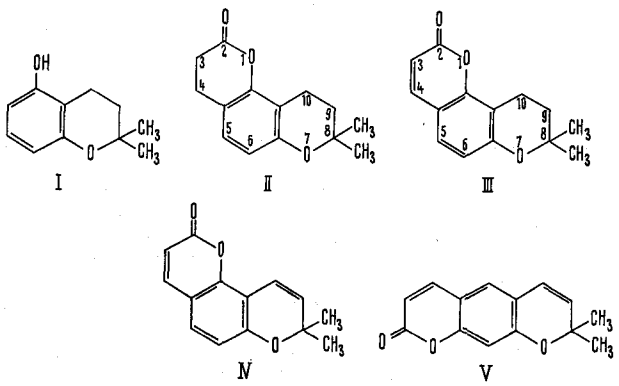
Synthesis of Seselin and its Hydroderivatives[1]

Seselin (IV) was isolated in 1936 together with bergapten and isopimpinellin from the fruits of *Seseli indicum* by BOSE and GUHA[2,3] and its structure was later established by degradation[3] and synthesis[4]. For the synthesis of seselin[4] the dimethyl chromene ring was developed on umbelliferone when the isomeric linear compound xanthyletin (V) was obtained as a by-product. In this communication we wish to report a new method for the synthesis of seselin (IV) via dihydroseselin (III) and tetrahydroseselin (II) in which the α-pyrone ring has been developed on the dimethylchroman nucleus.

Recently we have described[5,6] the building up of a coumarin ring by the $AlCl_3$ catalyzed reaction of methyl acrylate with the appropriate phenol and subsequent dehydrogenation. Grignard reaction of 5-acetoxy-3,4-dihydrocoumarin[5] with excess methyl magnesium iodide yielded 5-hydroxy-2,2-dimethyl chroman (I) in one step [mp 122–123° (lit.[7] mp 122°). Found: C, 73.70; H, 7.86. $C_{11}H_{14}O_2$ requires: C, 74.13; H, 7.92%]. In a manner similar to the experiments described earlier[6], condensation of (I) with methyl acrylate and $AlCl_3$ failed to produce the tetrahydroseselin (II) as expected, instead a substantial quantity of the polymerized product was isolated. However, using acrylonitrile and $ZnCl_2$ in the cold according to the procedure of ADAM's et al.[8] we succeeded in obtaining tetrahydroseselin [II, mp 105–106° (lit.[9] mp 106–107°),



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IR 1760 (lactone), 1620, 1590 (aromatic), 1135 (C–O–C) cm^{-1}, NMR δ ppm ($CDCl_3$), 6.99, 6.88 (1H, each, due to H-5 and H-6, J = 8Hz), 2.8 (2H, each, m, due to H-3, H-4 and H-10), 1.78 (2H, t, due to H-9, J = 7Hz), 1.32 (6H, s, gem dimethyl), found: C, 71.96; H, 6.96. $C_{14}H_{16}O_3$ requires: C, 72.39; H, 6.94%]. The compound II was dehydrogenated with Pd-C (10%) in boiling diphenyl ether to give dihydroseselin [III, mp and mmp[10] 102–103° (lit.[11] mp 103–104°), IR 1730 ($\alpha\beta$-unsaturated lactone), 1600, 1490 (aromatic), 1120 (C–O–C), cm^{-1} (Nujol), UV λ_{max}^{EtOH} 222, 247, 258, 328 (log ε 4.1, 3.6, 3.5 and 4.3), NMR δ ppm ($CDCl_3$) 7.60, 6.20 (1H each, d, due to H-4 and H-3, J = 10Hz), 7.20, 6.70 (1H each, d, due to H-5 and H-6, J = 9Hz), 2.90, 1.85 (2H each, t, due to H-9 and H-10), 1.36 (6H, s, gem dimethyl), found: C, 73.40; H, 6.07. $C_{14}H_{14}O_3$ requires: C, 73.02; H, 6.13%]. Dihydroseselin (III) on further dehydrogenation with DDQ[12] in dioxan yielded seselin (IV) mp 113–114° (depression in mp with dihydroseselin). Found: C, 73.42; H, 5.70. $C_{14}H_{12}O_3$ requires: C, 73.67; H, 5.30%. Further work is in progress and more details will be published in due course[13].

Zusammenfassung. Die Synthese des Naturstoffes Tetrahydroseselin aus der Frucht *Seseli indicum* wird beschrieben.

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A New Indian Source of Diosgenin (*Costus speciosus*)

In an extensive survey of 19 different species of Indian *Dioscorea* plants, Chakravarti et al.[1] found *Dioscorea prazeri* (*Kukur torul*) of Darjeeling and *Dioscorea deltoidea* (*Kins*) of Kashmir to be 2 rich sources of diosgenin. The yield of diosgenin was 2.1% from the former and 3.35% from the latter on the basis of dried yams. We have recently found a new source of diosgenin in the rhizomes of *Costus speciosus* which contains about 86.3% moisture. The alcoholic extract of the dried rhizomes on acid hydrolysis yields about 3.86% total sapogenins which on further crystallization and chromatography yields about 2.12% pure diosgenin (dry rhizomes). The diosgenin content of *Costus speciosus* compares favourably with that of *D. prazeri*, and can be utilized as a convenient commercial source for isolation of diosgenin. The main advantage of *C. speciosus* over the 2 species of *Dioscorea* is that *C. speciosus* grows abundantly in the plains, whereas both *D. prazeri* and *D. deltoidea* grow only at high altitudes of the Himalayas.

Costus speciosus (Koenig) Sm (N.O. Zingiberacea) (Sanskrit: *Kemuka*)[2] is a common plant with tuberous rhizome distributed throughout India, particularly in Bengal and Konkan. From a pharmacological study, Tewari et al.[3] reported that the fresh juice of the rhizomes of *C. speciosus* increased the tone, amplitude and frequency of rhythmic contractions of isolated uterus of rat, guinea-pig, rabbit, dog and human. The spasmodic activity was not blocked by atropine sulphate and pentolinium bitartrate. In view of the above uterine activity of the plant and its use as an ecbolic in the indigenous systems of medicine, a detailed chemical investigation was undertaken to isolate the active principles.

A systematic chemical and pharmacological study indicated that the chloroform extract of dried powdered rhizomes, after being extracted with petroleum ether and benzene, possessed the most potent and direct stimulant action on isolated uterus. This extract was found to contain a mixture of 5 saponins of varying proportions as revealed by thin-layer chromatography (TLC). Partition chromatography over silica gel followed by repeated crystallization from alcohol could separate the mixture broadly into 2 groups of saponins. The earlier crops of saponins of higher Rf values (0.76 and 0.55, $CHCl_3$:EtOH, 7:3) had either relaxant action or no specific response, whereas the later crops of saponins of lower Rf values (0.20, 0.14 and 0.06, $CHCl_3$:EtOH, 7:3) had direct stimulant action on isolated uterus. On TLC plates the colour of the upper 2 saponins changed from pink to grey and that of the lower 3 saponins from pink to green on developing with an alcoholic solution of acetic anhydride and sulphuric acid, indicating the presence of 2 different types of saponins.

The following 2 saponins could be isolated from the chloroform extract of the dried powdered rhizomes of *C. speciosus*: Saponin A, granules, mp 289–290° (80% alcohol), Rf 0.71 ($CHCl_3$:EtOH, 7:3). (Found[4]: C, 72.02, 72.13; H, 10.09, 10.27.) On acid hydrolysis it gave glucose and β-sitosterol ($C_{35}H_{60}O_6$ requires: C, 72.91; H, 10.41), and had no specific response on isolated uterus.

Saponin B, granules, mp 305–307° (80% alcohol), Rf 0.43 ($CHCl_3$:EtOH, 1:1). (Found[5]: C, 58.72, 58.80; H, 9.02, 9.19.) On acid hydrolysis the saponin yielded diosgenin, glucose and rhamnose.

The alcoholic extract of the fresh moist rhizomes of *C. speciosus* yielded the following saponin: Saponin C,

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