significant peaks are at m/e 300 (M^+, 75%), 193 (50%), 167 (100%), 166 (57%) and 107 (41.5%).

The compounds **3** (mp 147–148°) and **5** (mp 141–144°) were synthesized by condensing the corresponding chroman-4-ones with *p*-methoxy-benzaldehyde in dry HCl and acetic acid. Catalytic hydrogenation of **3** and **5** with Raney-Ni in ethanol led to racemic **8** (mp 99–100°) and racemic **10** (amorphous) respectively. The IR- and NMR-spectra of the synthetic materials **8** and **10** were identical with those of the permethylated derivatives of the natural products **6**, **7** and of **9** respectively.

With the compounds described in this paper 10 members of the new family of the homo-isoflavones are now known. They differ from each other not only by variations in the oxygenation and methylation patterns of the aromatic rings but also by varying states of oxidation at C-3 and C-9. The biogenetic implications of these findings are being investigated[8,9].

Zusammenfassung. Aus den Zwiebeln von *Eucomis punctata* L'Hérit. (Liliaceae) wurden 5 neue Homoisoflavone isoliert und ihre Struktur aufgeklärt.

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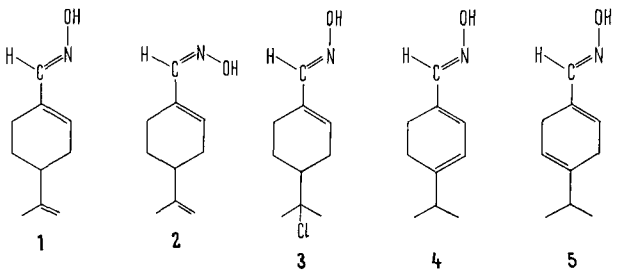
[9] We are indebted to Dr. W. Vetter, F. Hoffmann-La Roche & Co. A.G., Basel, for the mass spectra.

Perillartine and Some Derivatives: Clarification of Structures

The sweetening agent perillartine is the α-*syn*-oxime **1** of perillaldehyde, and should be recognized as the *syn* isomer, though it is commonly called '*α-anti*' in commerce and in review literature. The designation '*α-anti*' is inconsistent in terms of modern nomenclature and derives from the work of Furukawa and Tomizawa[1], published at a time when the true structure of α-oximes[2] as *syn* isomers and of β-oximes[2] as *anti* isomers was just becoming clear. Earlier, the reverse correlation was accepted, and the resultant confusion and error in names has persisted in the case of perillartine. Sometimes the correct (*syn*) structure is given[3] despite the name *α-anti*, but sometimes[4] in consequence the wrong (*anti*) structure **2** is drawn. The true *syn* structure of perillartine is now nicely confirmed by the elegant NMR technique[5] which states that for aldoximes in dimethylsulfoxide-d_6 solution, the difference $^{\delta}$NOH–$^{\delta}$CH=N is $\simeq$ 3 ppm for *syn* isomers and $\simeq$ 4 ppm for *anti* isomers. For perillartine, this difference is 3.02 ppm.



1 **2** **3** **4** **5**

It was claimed[1] that the β-isomer of perillartine (called 'β-syn', but predictably the *anti* isomer **2**) was formed conventionally through the HCl salt of **1** and was tasteless – unlike **1**, said to be 2000 times sweeter than sugar. This result has been cited[6] (with some confusion in names) as an example of striking difference in taste properties of geometrically isomeric oximes. However, reinvestigation has now shown that the compound obtained on attempted isomerization of perillartine **1** is not **2**, but rather the *tert*-chloride **3**, formed by Markovnikov addition of the elements of HCl to the isopropenyl group.

When D,L-perillartine **1** in methanol solution was treated with hydrogen chloride, addition of ether precipitated the hydrochloride[7] of **3**, mp 127–129°, $C_{10}H_{17}Cl_2NO$, with one ionic Cl. Treatment of an aqueous slurry of the salt with sodium carbonate, or with 1 *M* sodium hydroxide, generated 4-(2-chloro-2-propyl)-1-cyclohexene-1-carboxaldehyde *syn*-oxime **3**, mp 133–134°, $C_{10}H_{16}ClNO$, no ionic Cl (mp 129° was reported[1] for the product called the β-isomer). Alternatively, upon solution of perillartine in concentrated hydrochloric acid, dilution with water precipitated **3**. The structure was confirmed in the NMR-spectrum ($CDCl_3$ solutions) by the absence of the isopropenyl signals of perillartine (i.e., narrow doublets at δ 4.75 and 1.74 for $=CH_2$ and $CH_3C=$, respectively, J = 1.0 Hz) and by the appearance of a 6-proton singlet at δ 1.53 (CH_3–CCl–CH_3). Identical signals in both **1** and **3** were observed for the olefinic ring proton (δ 5.95–6.15) and for the oxime CH=N (singlet, δ 7.71). It was clear that no isomerization of the oxime group had occurred, and the difference $^{\delta}$OH–$^{\delta}$CH for **3** in dimethylsulfoxide-d_6 of 2.99 ppm confirmed that **3** was a *syn*-oxime.

In a further attempt to form the *anti*-oxime **2**, perillartine **1** was treated with BF_3 by the procedure of Hauser and Hoffenberg[8]. A pure isomer, mp 54–57°, was obtained after 1–2 days, but was shown to be the

[1] S. Furukawa and Z. Tomizawa, J. Chem. Ind. Tokyo *23*, 342 (1920); Chem. Abstr. *14*, 2839 (1920).

[2] The α-, β- differentiation of isomeric oximes was based on a comparison of chemical properties; cf. N. V. Sidgwick, I. T. Millar and H. D. Springall, *The Organic Chemistry of Nitrogen*, 3rd edn. (Oxford, London 1966), p. 322.

[3] *The Merck Index*, 7th edn. (Merck and Co., Rahway, New Jersey), p. 786.

[4] Beilstein, *Handbuch der Organischem Chemie* (Springer-Verlag, Berlin, Heidelberg 1968), vol. 7, 3rd suppl., p. 566.

[5] G. G. Kleinspehn, J. A. Jung and S. A. Studniarz, J. org. Chem. *32*, 460 (1967).

[6] L. N. Ferguson and E. R. Lawrence, J. chem. Educ. *35*, 436 (1958). – K. Kulka, J. Agr. Food Chem. *15*, 48 (1967).

[7] Treatment of an ether solution of **1** with HCl gave only partial conversion to a hydrochloride, co-precipitated with **1**; by this means Furukawa and Tomizawa reported a hydrochloride, mp 114°, which upon basification gave the oxime of mp 129° (resumably **3**).

[8] C. R. Hauser and D. S. Hoffenberg, J. org. Chem. *20*, 1491 (1955).

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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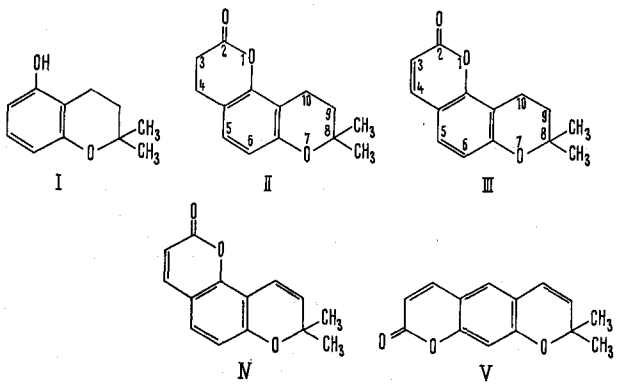
[9] For the parent aldehyde of **4**, λ_{max} 315 nm (ε 15,600), according to H. KAYAHARA, H. UEDA, I. ICHIMOTO and C. TATSUMI, J. org. Chem. *33*, 4536 (1968).

[10] E. M. ACTON, H. STONE, M. A. LEAFFER and S. M. OLIVER, to be published.

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°),



[1] Part X of a series *Coumarins and Related Compounds*. Part IX, A. K. DAS GUPTA, R. M. CHATTERJE and K. R. DAS, J. chem. Soc. (C), (1969), 2618.

[2] P. K. BOSE and N. C. GUHA, Sci. Cult. *2*, 326 (1936).

[3] E. SPÄTH, P. K. BOSE, J. MATZKE and N. C. GUHA, Chem. Ber. *72B*, 821 (1939).

[4] E. SPÄTH and R. HILLEL, Chem. Ber. *72B*, 963 (1939); *72B*, 2093 (1939).

[5] A. K. DAS GUPTA, R. M. CHATTERJE, K. R. DAS and B. GREEN, J. chem. Soc. (C) (*1969*), 29.

[6] A. K. DAS GUPTA and K. R. DAS, J. chem. Soc. (C) (*1969*), 33.

[7] R. HULS, Bull. Acad. Belg. *39*, 1064 (1953).

[8] W. D. LANGLEY and R. ADAMS, J. Am. chem. Soc. *44*, 2320 (1922).

[9] E. SPÄTH and O. NEUFELD, Chem. Ber. *71*, 353 (1938).