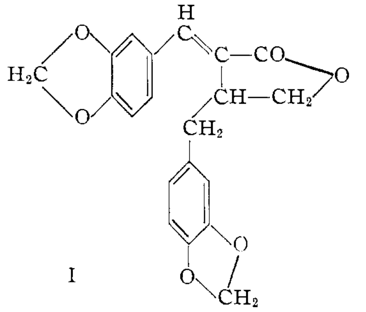
Identity of Hibalactone and Savinin

By Mitsuo Masumura and F. Shigeo Okumura

Received December 2, 1954

One of us has reported[1] that hibalactone (I), $C_{20}H_{16}O_6$, m.p. 146–146.5°, $[\alpha]^{23}D$ −87° (chloroform), isolated from young leaves of chyabohiba, nikohiba or *Chamaecyparis obtusa* (Cupressiacenae),[2] has the structure shown in Cmpd. I. This structure was established by the production of piperonylic acid, piperonal and oxalic acid either by permanganate oxidation or ozonolysis, by hydrogenation (Raney nickel or sodium amalgam) to (+)-isohinokinin[3] (major product) and (−)-hinokinin[3] (minor product) by spectroscopic evidence pointing to an α,β-unsaturated lactone structure, and by studies of the hydrolysis, nitration and bromination products of I.



I

Independently of these studies on hibalactone, the structure of savinin, m.p. 146.2–147.3°, $[\alpha]^{22}D$ −88° (chloroform), isolated from the dried needles of *Juniperous sabina*, was reported by Schrecker and Hartwell,[4] and we found, quite unexpectedly, that its structure coincides with that of hibalactone. A comparison of the properties of these two substances and their derivatives is given in Table I.

Table I

Comparison of Savinin and Hibalactone

	Savinin, λ_{max}^{EtOH} 334, 293, 237			Hibalactone, λ_{max}^{EtOH} 333, 292, 237		
	M.p., °C.	$[\alpha]^t D$	t, °C.	M.p., °C.	$[\alpha]^t D$	t, °C.
Pure	146.2–147.3	− 88°[a]	22	146–146.5	− 87°[a]	23
Dibromide				181–182	−108[c]	28.5
Tetrabromide				238–239		
Dinitro deriv.				247–248	+157[d]	28.5
Mononitro deriv.				164–165	+143[c]	29
Lactonic acid	108	+ 64[b]	20	107		
Dihydro derivs.	116.3–116.7	+107[a]	21	116–117	+106[e]	19
Isodihydro deriv.				63–64	− 33[a]	19

[a] Chloroform. [b] Ethanol. [c] Benzene. [d] Pyridine. [e] Acetone.

A sample of savinin kindly provided by Dr. Schrecker gave no depression of m.p. when mixed with I, and the infrared spectra[5] of the two substances in chloroform solution showed no significant differences. Therefore, it is concluded that savinin and hibalactone are identical.

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(1) M. Masumura, *J. Chem. Soc. Japan*, in press. Presented in part at the 7th General Meeting of the Chemical Society of Japan, Tokyo, April 4, 1954.

(2) "Chyabohiba" is a garden kind of *Chamaecyparis obtusa* and "nikohiba" is a garden kind of *Chamaecyparis pisifera*.

(3) S. Keimatsu and T. Ishiguro, *J. Pharm. Soc. Japan*, **56**, 103, 901 (1936).

(4) A. W. Schrecker and J. L. Hartwell, This Journal, **76**, 4896 (1954).

(5) Kindly determined by S. M. Aronovic, Department of Chemistry, University of Wisconsin, on a Baird Associates, Inc., Spectrophotometer.

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Transformation of D-Allose to 1,6-Anhydro-β-D-allopyranose in Acid Solution[1,2]

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Received December 9, 1954

It has been recognized for some time that when sugars having the *altro* or *ido* configuration are heated in dilute aqueous acid an equilibrium is established in which a considerable part of the carbohydrate is present in the form of a monomeric non-reducing anhydride.[3] More recently the *gulo* configuration[2,3a] has been added to the list, and in addition it has been established that D-glucose is converted to levoglucosan (1,6-anhydro-β-D-glucopyranose) to a very limited extent under these conditions.[4]

We have extended the study of this reaction to include the *allo* configuration and now wish to report that when D-allose (I) is heated in dilute aqueous acid an equilibrium is established in which 1,6-anhydro-β-D-allopyranose (II) is present to the extent of approximately 14%. Isolation and crystallization of the anhydride were readily accomplished and the new compound melts at 179–180° and shows $[\alpha]^{20}D$ −76° in water.

In order to establish the structure of the new anhydride, we first oxidized with periodate in the usual manner. The consumption of two molar equivalents of oxidant and the liberation of one molar equivalent of acid were unequivocal evidence of the presence in the anhydride of three contiguous secondary hydroxyl groups. The resulting dialdehyde was oxidized further with bromine, and the sodium salt of the dibasic acid III condensed with *p*-phenylphenacyl bromide. A crystalline diester was obtained whose physical constants, including a mixed melting point, were in agreement with those reported for the compound obtained similarly from levoglucosan.[2] Since the structure of levoglucosan is well established, our new anhydride must have the analogous structure of 1,6-anhydro-β-D-allopyranose.

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(1) Presented in part before the Division of Carbohydrate Chemistry at the New York Meeting of the American Chemical Society, September 17, 1954; see Abstracts of Papers, page 22D.

(2) For the preceding paper on anhydro sugars, see L. C. Stewart and N. K. Richtmyer, This Journal, **77**, 1021 (1955).

(3) (a) L. C. Stewart and N. K. Richtmyer, *ibid.*, **77**, 424 (1955); (b) J. W. Pratt, N. K. Richtmyer and C. S. Hudson, *ibid.*, **75**, 4503 (1953).

(4) A. Thompson, K. Anno, M. L. Wolfrom and M. Inatome, *ibid.*, **76**, 1309 (1954); L. D. Ough and R. G. Rohwer, Abstracts of Papers, New York Meeting of the American Chemical Society, Sept. 12–17, 1954, page 16D.