Tetrahedron Letters No.20, pp. 1227-1231, 1964. Pergamon Press Ltd.
Printed in Great Britain.

STRUCTURE OF TAURANIN

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(Received 16 March 1964)

One of us (H.N.) had isolated a colorless crystal, oosporin,[1] and two yellow pigments, aurantin[1] and tauranin[2] from the mycelia of Oospora aurantia (Cooke) Sacc. et Vogl., a mold which grows on seeds of Thea japonica. The structure of tauranin has now been established as being 1, whereas aurantin, mp. 180°(d.), has been found by thin-layer chromatography to be a mixture of tauranin and a colorless unidentified substance. Pertinent reactions and physical constants are summarized in the Scheme and Table.

The UV spectrum of tauranin(1), $C_{22}H_{30}O_4$, is characteristic of monohydroxy-p-benzoquinones[3]. Upon catalytic reduction there is produced an epimeric mixture of dihydrodeoxytauranins(2); only the minor epimer 2b could be obtained in pure form. Acetylation of both epimers gave the corresponding acetates 3a and 3b; a reductive triacetate 4a having benzenoid UV absorption was prepared from the acetate 3a. The fact that

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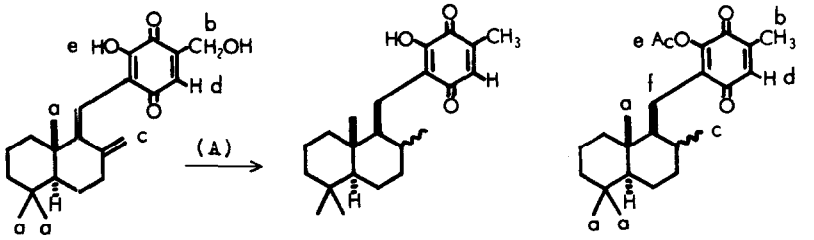
SCHEME

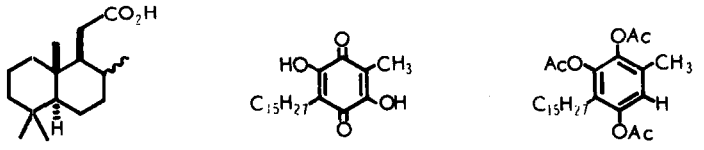


1 mp. 155°(d.)
λ_{max}^{MeOH} 266, 415
(4.07, 3.07)

2 epimeric mixture
mp. 159-61°

2a major epimer —(B)→ 3a mp. 136°

2b minor epimer —(B)→ 3b mp. 158-60°
mp. 170°(d.)



6(=13) eutectic mixture of epimers
mp. 108-9°

5b mp. 257-9°
$\nu_{max}^{CHCl_3}$ 3375, 1631
λ_{max}^{EtOH} 298, 445
(4.28, 2.32)

4a mp. 123-4°
λ_{max}^{EtOH} 267
(2.65)

Reagents: (A) H_2 over Pd/C followed by aerial oxidation; (B) Ac_2O-AcONa; (C) Zn-Ac_2O-AcONa; (D) $PhNH_2$ followed by H^+; (E) O_3

Small alphabets by protons refer to the NMR Table.

IR data in cm^{-1}; UV data in mμ(log ε).

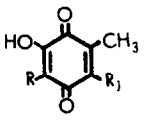
the hydroxymethyl group in tauranin, which suffers hydrogenolysis, is adjacent to the ring proton is evident from the change in the NMR peaks of the b and d protons (Table); i.e., the 4.53 (2H, doublet)/6.65 ppm (1H, triplet) set of peaks in the spectrum of tauranin(1) were converted to the 2.04 (3H, doublet)/6.58 ppm (1H, quartet) and 2.04 (3H, doublet)/6.61 ppm (1H, quartet) set of peaks in the spectra of the acetates 3a and 3b, respectively. A choice between the two substitution patterns, 8 and 9 in 2, was made by introducing a hydroxyl group into the ring as in 5b. It has recently been reported[4] that dihydroxybenzoquinones of the types 10 and 11 can be differentiated readily by their IR bands; in $CHCl_3$, type 10

TABLE

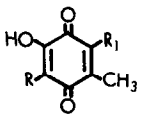
NMR Peaks of Tauranin and Derivatives

		1	3a	3b
CH_3	a	0.76, 0.81, 0.86	0.83, 0.83, 0.89	0.81, 0.83, 0.87
CH_2OH or CH_3	b	4.53(d, 1.2)	2.04(d, 1.5)	2.04(d, 1.6)
$=CH_2$ or CH_3	c	4.67	0.96(d, 7)	0.75(d, 4)
Ring H	d	6.65(t, 1.2)	6.58(q, 1.5)	6.61(q, 1.6)
OH or OAc	e	7.05(br)	2.33	2.34
CH_2	f	unclear	~2.5(m)	~2.3(m)

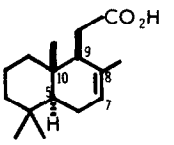
Values in ppm from internal TMS, Varian A-60, $CDCl_3$ solution, singlets unless otherwise stated.
Abbreviations: d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.
Figures in ( ) are J constants expressed in cps.
Integrated intensities of peaks were in agreement with number of protons.



8 R_1:H
10 R_1:OH



9 R_1:H
11 R_1:OH



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has absorptions at 3350 and 1635 cm^{-1}, whereas type 11 has absorptions at 3480 and 1650 cm^{-1} (doublet). The derivative 5b clearly belonged to type 10.

Presence of a terminal methylene group in tauranin(1) is indicated by the conversion of the two-proton 4.67 ppm singlet c in 1 to a three proton doublet c in the acetates 3a and 3b (0.96 and 0.75 ppm).

The C_{16}-acid 6 was obtained by ozonolysis of the hydrogenation product 2. The $\Delta^{7,8}$-acid 12* obtained from ambrein and sclareol was hydrogenated over Adams' catalyst to give the known acid 13[5] melting at 107-107.5°. This acid was identical in every respect (including ORD) with the acid 6 derived from tauranin. Since the stereochemistry of ambrein and sclareol is established[6,7], and since the acid 12 is prepared by routes not affecting the optical centers at C-5, C-9 and C-10, the structure of tauranin is established as shown in 1.

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* We are greatly indebted to Dr. M. Stoll, Firmenich und Cie, Geneve, Switzerland, for a gift of this acid. We also thank Dr. J. Polonsky, Institut de Chimie des Substances Naturelles, Gif-sur-Yvette, France, for a gift of the 8α-hydroxy-8β-methyl acid.

Tauranin is biogenetically unique in that it is the first acetogenin-derived benzoquinonoid to which there is attached a cyclized isoprenoid.

The acid 13(= 6) has been found to be an eutectic mixture of 8α and 8β epimers. Furthermore, the isomeric acid with mp. 112-114° obtained from ambrein and sclareol[8] is the 8α-epimer, while the acid with mp. 128° from ambrein and manool[6] is the 8β-epimer[9]. Details will be reported in a full paper.

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