78.12; H, 6.64; N, 6.79. IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1259, 1087, 1037 (C-O-C). UV λ_{max}^{EtOH} mμ (log ε) : 214 (4.29), 229.5 (4.69), 286 (3.72), 292 (3.75), 302.5 (3.66), 310 (3.50), 316 (3.36). NMR : see Fig. 3.

2,2,4-Trimethyl-2,3-dihydrofuro[3,2-*c*]quinoline (IIIb)——A mixture of 0.4 g. of IIb and 0.25 g. of pyridine·HCl was treated as above and the resulting crystalline product was recrystallized from petr. benzin to yield 0.35 g. of colorless pillars, m.p. 96~97°. *Anal.* Calcd. for $C_{14}H_{15}ON$: C, 78.84; H, 7.09; N, 6.57. Found : C, 78.99; H, 7.23; N, 6.77. IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1287, 1080, 1020 (C-O-C). UV λ_{max}^{EtOH} mμ (log ε) : 214 (4.51), 229.5 (4.73), 285 (3.76), 292 (3.80), 302.5 (3.71), 309.5 (3.59), 315.5 (3.42). NMR : see Fig. 3.

2,3,4-Trimethyl-2,3-dihydrofuro[3,2-*c*]quinoline (IIIc)——A mixture of 0.4 g. of IIc and 0.25 g. of pyridine·HCl was treated as above and the resulting crystals were recrystallized from petr. benzin to give 0.41 g. of colorless prisms (IIIc), m.p. 74.5~75.5°. *Anal.* Calcd. for $C_{14}H_{15}ON$: C, 78.84; H, 7.09; N, 6.57. Found : C, 78.75; H, 7.18; N, 6.73. IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1253, 1090, 1020 (C-O-C). UV λ_{max}^{EtOH} mμ (log ε) : 214 (4.48), 230 (4.75), 285.5 (3.76), 291.5 (3.79), 302 (3.69), 308 (3.57), 315 (3.37). NMR : see Fig. 3.*6

The author expresses his gratitude to Prof. Emeritus E. Ochiai of the University of Tokyo, Dr. K. Takeda, Director of this Laboratory, and Dr. H. Kano, for their encouragement. Thanks are also due to Mr. S. Notzumoto for his technical assistance, to the members of the Physical Chemistry Department for the IR, UV, and NMR spectral measurements, and to the members of the Analysis Room for the elementary analysis.

Summary

The thermal rearrangement of allyl, methallyl, and crotyl ethers (Ia, Ib, and Ic) of 2-methyl-4-quinolinol was investigated and the *ortho*-Claisen rearrangement products (IIa, IIb, and IIc) with the inversion of the migrating group and their consecutive intramolecular cyclization products, the 2,3-dihydro[3,2-*c*]quinoline derivatives (IIIa, IIIb, and IIIc) were obtained. No detectable amounts of the 1-allyl-2-methyl-4(1*H*)-quinolones resulting from the alkyl rearrangement were formed. The different results between the thermal rearrangement of the allyl 2-methyl-4-quinolyl ethers and that of the 7-allyloxy-*s*-triazolo[1,5-*a*]pyrimidines were discussed.

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113. Kenya Kawashima,*1 Koji Nakanishi,*2 and Hidejiro Nishikawa*3 : Structure of Tauranin and a Note on the "C_{16}-Acids" obtained from Di- and Triterpenoids.*4

(*Department of Chemistry, Tokyo Kyoiku University,*1 *Department of Chemistry, Tohoku University,*2 *and College of Agriculture and Veterinary Medicine, Nihon University*3)

One of us (H.N.) had isolated three crystals, designated oosporin, aurantin,[1] and tauranin[2] from the mycelium of *Oospora aurantia* (Cooke) Sacc. et Vogl., a mold that grows on seeds of *Thea japonica.* The evidence given below enables one to establish

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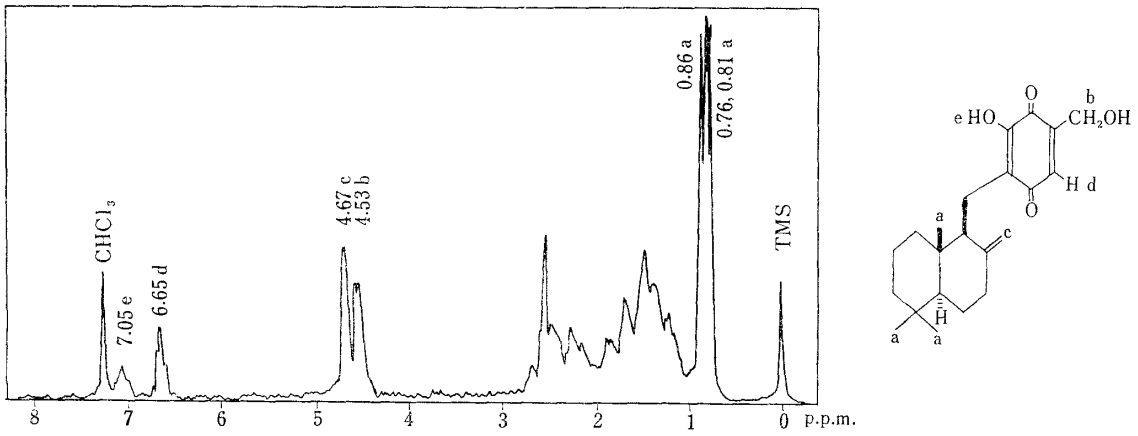
*3 Setagaya, Tokyo (西川英次郎).

*4 Part of the present studies has been reported in a preliminary communication : K. Kawashima, K. Nakanishi, M. Tada, H. Nishikawa : Tetrahedron Letters, **1964**, 1227.

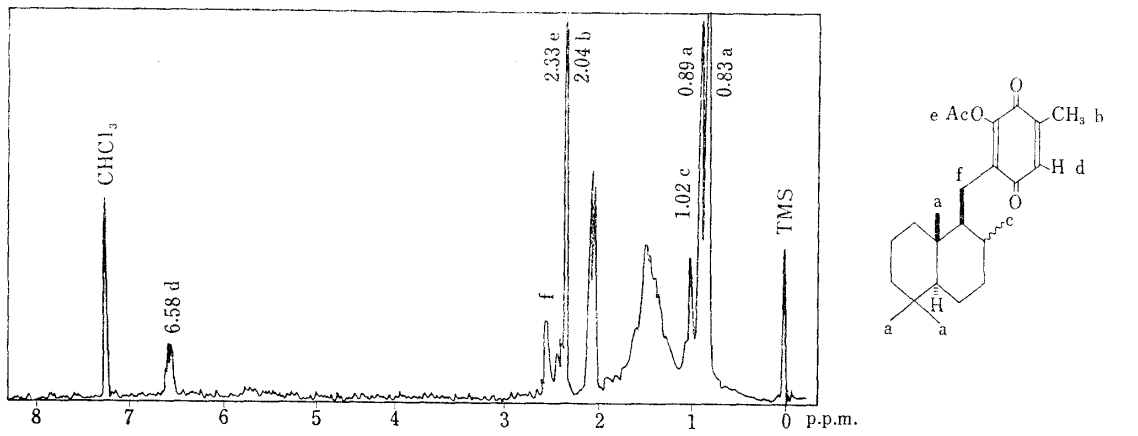
1) H. Nishikawa : Proc. Imp. Acad. (Tokyo), **10**, 414 (1934).

2) *Idem* : Trans. Tottori Soc. Agr. Sci., **9**, 1 (1949).

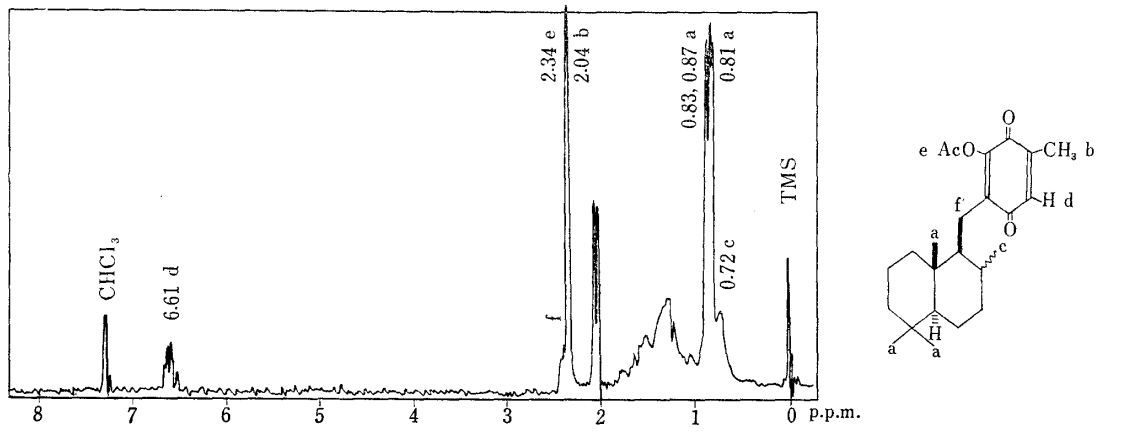
the total structure of tauranin as I. On the other hand, "aurantin" gave two spots on the thin-layer chromatogram; the higher one was yellow and corresponded to that of tauranin, while the lower spot was colorless. Since tauranin could be separated from "aurantin" by column chromatography on silicic acid or by extraction with sodium phosphate and reacidification, it follows that aurantin is a mixed crystal of two compounds, one of which is tauranin. An attempt to isolate the colorless component failed because of its facile decomposition.



a) Tauranin (I)

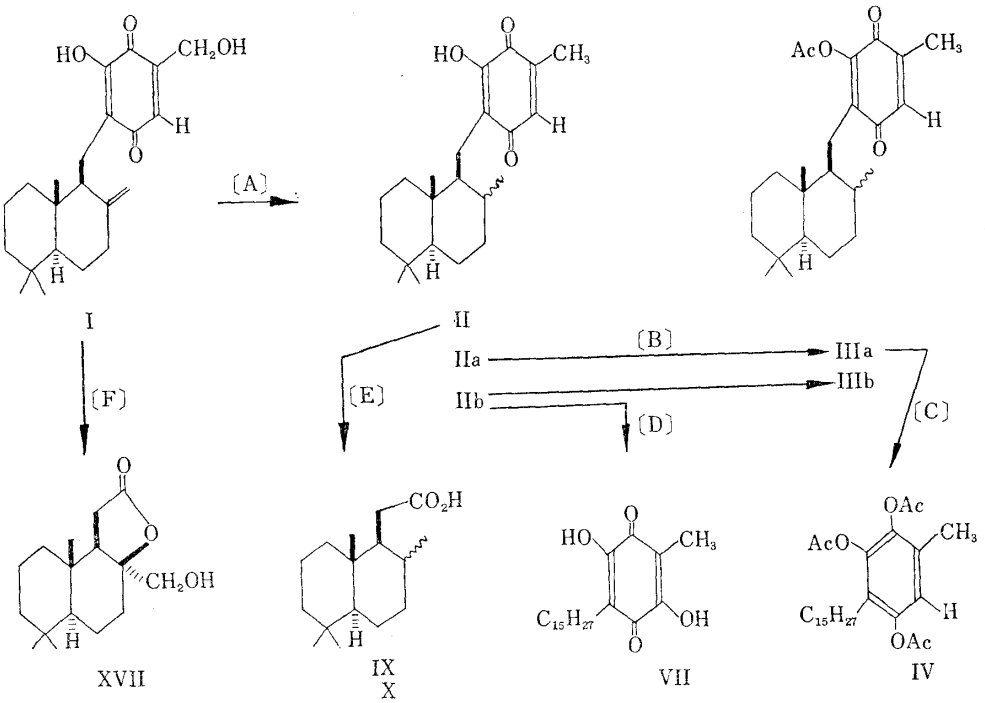


b) Dihydrodeoxytauranin acetate (IIIa)



c) *epi*-Dihydrodeoxytauranin acetate (IIIb)

Fig. 1. Nuclear Magnetic Resonance Spectra of Tauranin and Derivatives, in Deuterochloroform, 60 Mc, p.p.m. from TMS



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 [F] H_2O_2/OH^-

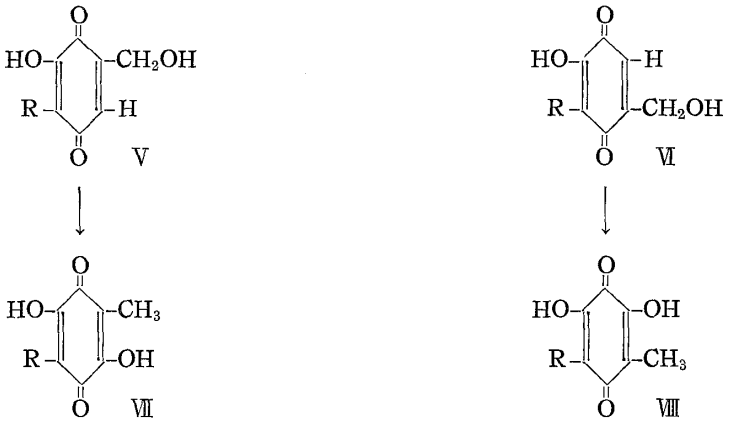
Chart 1.

Tauranin (I) $C_{22}H_{30}O_4$, is a quinone as suggested by its decoloration with sodium dithionite and by its ultraviolet absorption, λ_{max}^{MeOH} mμ (log ε) : 266 (4.07), 415 (3.07), which is characteristic of monohydroxy-*p*-benzoquinones.[3]

Tauranin absorbed 3 moles of hydrogen when hydrogenated over palladium-charcoal; after aerial oxidation, there was obtained crystals of the dihydrodeoxytauranins (II), which was later found to be an eutectic mixture of epimers. It was possible to isolate the minor constituent, *epi*-dihydrodeoxytauranin (IIb) in pure form after repeated recrystallizations. The two epimers both gave the corresponding monoacetates (IIIa) and (IIIb). The nuclear magnetic resonance spectra of tauranin (I) and the two acetates (IIIa) and (IIIb) are recorded in Fig. 1. The oxygen atom removed during the hydrogenation step is that of a hydroxymethyl group as seen by the replacement of the two-proton doublet at 4.53 p.p.m. (J=1.2 c.p.s.) in Fig. 1a by the three-proton doublets at 2.04 p.p.m. (J=1.5 and 1.6 c.p.s.) in Figs. 1b and 1c (peak b). In agreement with the presence of an adjacent quinonoid proton, the triplet at 6.65 p.p.m. (J=1.2 c.p.s.) in Fig. 1a is converted to the quartets at 6.58 (J=1.5 c.p.s.) and 6.61 p.p.m. (J=1.6 c.p.s.), respectively in Figs. 1b and 1c (peak d). The $\nu_{C=O}$ bands of the acetates (IIIa) and (IIIb) at 1787 and 1788 cm^{-1} (in CCl_4), respectively, together with peak e (hydroxyl bonded to quinonoid C=O) in Fig. 1a clearly indicated the presence of a hydroxyl attached to the quinonoid ring in tauranin. The acetate (IIIa) also gave a reductive triacetate (IV) having benzenoid ultraviolet absorption. Thus, tauranin has part structure (V) or (VI) (R=$C_{15}H_{25}$) (Chart 2).

Of the two possible structures (V) and (VI), the latter was excluded as follows. An additional hydroxyl group was introduced into the quinone ring of *epi*-dihydrodeoxytauranin (IIb) by allowing it to react with aniline to give an anilino-derivative,[4] which on subsequent hydrolysis yielded the dihydroxyquinone $C_{22}H_{32}O_4$, (VII) or (VIII) (R=$C_{15}H_{27}$),

3) W. Flaig, J. C. Salfeld : Ann. Chem., **618**, 117 (1958).
4) F. Kögl, A. G. Boer : Rec. trav. chim., **54**, 779 (1935).



IR ν_{max}^{KBr} cm^{-1} : 3320, 1615
$\nu_{max}^{CHCl_3}$ cm^{-1} : 3350, 1635

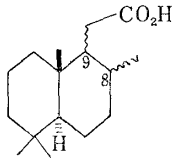
IR ν_{max}^{KBr} cm^{-1} : 3240, 1650 (doublet)
$\nu_{max}^{CHCl_3}$ cm^{-1} : 3480, 1650 (doublet)

Chart 2.

UV λ_{max}^{EtOH} mμ (log ε) : 298 (4.28), 445 (2.32). It has recently been shown[5,6] that dihydroxybenzoquinones of types (VII) and (VIII) can be readily differentiated by means of the characteristic infrared bands summarized in Chart 2. The dihydroxyquinone derived from tauranin absorbed at 3335 and 1611 cm^{-1} (KBr), or 3375 and 1631 cm^{-1} ($CHCl_3$), and this establishes the structure of the quinonoid moiety as being VII (R=$C_{15}H_{27}$), *i.e.*, V (R=$C_{15}H_{25}$) for tauranin itself. This is also in agreement with the biogenesis (see below).

The alicyclic portion of tauranin is discussed next. Three methyl singlets at 0.76, 0.81, and 0.86 p.p.m. are present in the nuclear magnetic resonance spectrum of tauranin (Fig. 1a). In addition, there is present an exocyclic methylene group, 4.67 p.p.m. which is converted into the secondary methyl groups at 0.96 (J=7 c.p.s.) and 0.75 p.p.m. (J=4 c.p.s.), respectively, in the dihydrodeoxy acetate spectra (peak c, only one component of the doublets can be seen clearly). Ozonolysis of the epimeric mixture of dihydrodeoxytauranins (II) gave an eutectic mixture of epimeric dihydrotauranic acids (IX), $C_{16}H_{28}O_2$, m.p. 108~109°; a minute amount of one epimer, m.p. 113.5~114.5° (X) was also isolated from the reaction mixture. Biogenetic considerations, in conjunction with the above-mentioned nuclear magnetic resonance methyl peaks, suggested that planar structure (XII) would be most plausible for these C_{16}- acids. That this indeed was the case

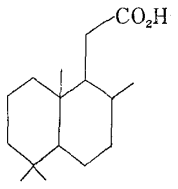
Table I. The C_{16}-Acids from Terpenoids

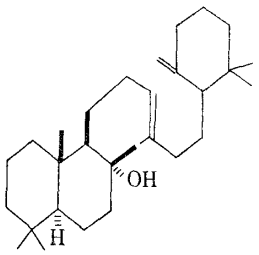


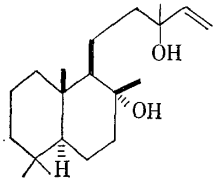
	Source	m.p. (°C)	$[\alpha]_D^{CHCl_3}$	Configuration
IX	XIII, XIV[7] and tauranin[a]	107~107.5	—	8α,9β+8β,9β[a]
X	XIII, XIV[8] and tauranin[a]	112~114	+68.5°	8α,9β[a]
XI	XIII and XV[9]	128	+10.8°	8β,9β[11]

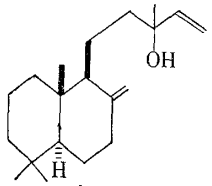
a) Present paper

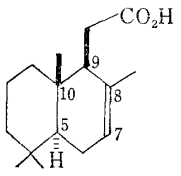
5) B. W. Bycroft, J. C. Roberts : J. Org. Chem., **28**, 1429 (1963).
6) S. Natori, H. Ogawa, K. Yamaguchi, H. Nishikawa : This Bulletin, **10**, 1343 (1963); S. Natori, H. Nishikawa, H. Ogawa : *Ibid.*, **12**, 236 (1964).
7) M. Stoll, M. Hinder : Helv. Chim. Acta, **37**, 1859 (1954).
8) C. C. Asselineau, E. Lederer, D. Mercier, J. Polonsky : Bull. soc. chim. France, 720 (1950).
9) L. Ruzicka, O. Dürst, O. Jeger : Helv. Chem. Acta, **30**, 353 (1947).


XII


XIII
ambrein


XIV
sclareol


XV
manool


XVI

was proven by direct comparison with an authentic sample, and this also established the whole stereochemistry. Three acids (Table I, IX, X, XI) having the structure (XII) have already been derived from ambrein (XIII), sclareol (XIV) and manool (XV). Of these acids, the one with m.p. 107~107.5° prepared by hydrogenation of the acid (XVI),[*5] which in turn had been prepared from ambrein and sclareol,[7] was in fact identical with the dihydrotauranic acids (IX) (mixed melting point, IR, ORD). Since the stereochemistry of ambrein (XIII) and sclareol (XIV) is firmly established,[9,10] and transformations leading to the acid (XVI) do not involve configurational changes at C-5, -9, and -10, the configurations at these centers in IX is established. Thus the structure of tauranin is also established as being I.

When the methyl ester of the acid (IX) (prepared by reacting with diazomethane) was subjected to gas chromatography, two peaks with relative intensities of 6:4 appeared; it is thus clear that the acid is an eutectic mixture of two acids epimeric at C-8. Furthermore, the methyl ester of the acid (X) had a retention time identical with the first peak of the ester mixture described above; the melting point of this acid (X) is identical with the acid previously derived from ambrein and sclareol.[8] Accordingly, the other isomer (XI), m.p. 128°, should correspond to the acid giving the second peak in the gas chromatogram, although a direct comparison has not been effected. Since the mode of formation of the acid (XI)[9] clearly shows that it has C-8β and C-9β configurations,[11] it follows that the acid (X) has C-8α and C-9β configurations (Table I).

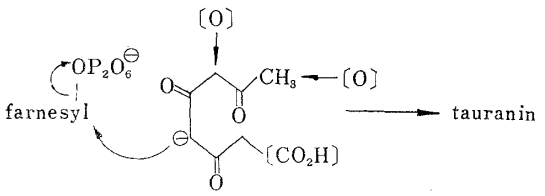


Chart 3.

Alkaline hydrogen peroxide oxidation of tauranin gave a hydroxy-γ-lactone, $C_{16}H_{26}O_3$, IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 3635, 3420, 1768, which can be formulated as XVII on the basis of a two-proton nuclear magnetic resonance singlet at 3.47 p.p.m. (e-CH_2OH, in $CDCl_3$).

Biogenetically, the structure of tauranin can be derived in a straightforward manner

*5 We are grateful to Dr. M. Stoll, Firmenich und Cie, Geneve, Switzerland, for a gift of the acid (XVI). We are also indebted to Dr. J. Polonsky, Institut de Chimie des Substances Naturelles, for a gift of its progenitor, the 8α-hydroxy-8β-methyl acid.

10) G. Büchi, K. Biemann : Croat. Chem. Acta, **29**, 163 (1957); J. D. Cocker, T. G. Halsall : J. Chem. Soc., **1957**, 4401.

11) *Idem* : *Ibid.*, **1956**, 4262.

from a farnesyl pyrophosphate unit and the orcinol type condensation of an acetogenin[12].

This scheme places the hydroxymethyl and isoprenoid groups para with respect to each other, and provides support for the conclusion reached by the infrared spectroscopic evidence described above. The naturally occurring benzoquinones, perezone[4] and helicobasidin[6] have structures that are built exclusively from C_5-units, whereas ubiquinones[13] and Kofler's quinone[14] have acyclic isoprenoid side-chains. Tauranin is unique in that it has a cyclic isoprenoid side-chain attached to an acetogenin-derived benzoquinone.

Experimental

UV : Hitachi EPS-2
IR : Japan Spectroscopic Company JASCO 301 and 401G (grating)
NMR : Unless otherwise stated, Varian A-60, in $CDCl_3$, values in p.p.m. relative to internal TMS. s, singlet; d, doublet; t, triplet; q, quartet; m, mulitplet.
ORD : Rudolph Photoelectric Spectro-Polarimeter Model 200S
GC : Wilkens A-700 Automatic Preparative Gas Chromatograph, Chromosorb P(45/60 mesh) coated with 30% SE-30, He carrier, flow rate 70 ml./min., column temperature 260°, detector temperature 290°, evaporation temperture 325°.

Aurantin——Crude aurantin extracted by Nishikawa[1] was further recrystallized from benzene-Et_2O to give fine gold yellow prisms, until no change in its IR spectrum was observed; m.p. 175~180°(decomp. after darkening at about 165°), $[\alpha]_D^{21}$ + 70.6° (MeOH, c=0.094), UV λ_{max}^{MeOH} mμ (log $E_{1cm}^{1\%}$) : 256 (2.37), 320 (1.74), 415 (1.23), IR $\nu_{max}^{CCl_4}$ cm^{-1} : 3670, 3620, 3445; $\nu_{max}^{CHCl_3}$ cm^{-1} : 2930, 1658, 1643, 1619, 1387, 1366, 1340, 898. Aurantin gave two spots on thin-layer chromatogram using silicic acid as absorbent and isopropyl ether as solvent; colorless spot, Rf 0.24, and yellow spot, Rf 0.84 (developed with Me_2CO solution of $KMnO_4$). The yellow spot corresponded to pure tauranin. Aurantin did not change its composition on further recrystallization. However, when the purification method for tauranin (see below) was applied to aurantin, tauranin was obtained. Tauranin was also obtained merely by chromatographing aurantin on silicic acid. The colorless component of aurantin is highly unstable and decomposes to a dark colored material, which has not been obtained in pure form.

Tauranin (I)——The crude sample of tauranin extracted by Nishikawa[2] was dissolved in Et_2O and shaken with 2.5% aq. sodium phosphate solution, when the aqueous layer turned violet and the yellow color of the Et_2O solution faded. Extraction was repeated until no coloration in the aqueous solution could be observed; at this stage the color of the Et_2O layer became dark brown. Acidification of the combined solution with 6*N* HCl gave an orange precipitate, which was again dissolved in Et_2O and the same processes were repeated several times. Further purification was effected by chromatography on silicic acid; elution with CH_2Cl_2 afforded pure tauranin, which crystallized as orange yellow thin prisms, m.p. 150~160°(decomp.), $[\alpha]_D^{21}$ −148°(MeOH, c=0.099), UV λ_{max}^{MeOH} mμ (log ε) : 266 (4.07), 415 (3.07), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3640, 3415 (OH), 1662 (sh), 1644, 1622 (CO, C=C), 2940, 1476, 1469, 1390, 1367 (CH_3, CH_2), 899 (quinone,=CH_2), NMR: (Fig. 1a) 0.76 (s CH_3), 0.81 (s CH_3), 0.86 (s CH_3), 1.0~2.8 (m CH_2CH), 4.53 (d J=1.2 c.p.s. CH_2O), 4.67 (s =CH_2), 6.65 (t J=1.2 c.p.s. ring H), 7.05 (broad s enolic OH), *Anal.* Calcd. for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44. Found : C, 73.65; H, 8.21. Tauranin was soluble in aqueous Na_2CO_3, and its purple color disappeared on addition of sodium dithionite.

Dihydrodeoxytauranins (II) and *epi*-Dihydrodeoxytauranin (IIb)——Tauranin (200 mg.) in MeOH (20 ml.) was hydrogenated at a room temperature and an atmospheric pressure in the presence of Pd-C (10%, 200 mg.). It took up 36.6 ml. (2.93 moles) of hydrogen after 24 hr. The resulting colorless solution was left standing overnight in the air, when the color turned yellow again. The catalyst was filtered off, the solvent evaporated and the crystalline residue chromatographed on silicic acid; an eluate with $CHCl_3$ afforded the epimeric mixture of dihydrodeoxytauranins (II), m.p. 159~161°, UV λ_{max}^{EtOH} mμ (log ε) : 267 (4.11), 420 (3.05), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3410 (OH), 1663, 1645, 1624, 894 (quinone), NMR: 0.74 (s a half of d $CHCH_3$), 0.83 (s $2CH_3$), 0.92 (s CH_3), 1.03 (s a half of d $CHCH_3$), 1.1~2.0 (m CH_2, CH), 2.04 (d J=1.5 c.p.s. ring CH_3), 2.2~2.7 (m CH_2 adjacent to quinone ring), 6.47 (q J=1.5 c.p.s. ring H), 6.93, 7.00 (OH).

12) R. W. Richards : "Recent Developments in the Chemistry of Natural Phenolic Compounds," (Edited by W. D. Ollis) 1 (1961). Pergamon, New York.
13) B. L. Lester, F. L. Crane, Y. Hatefi : J. Am. Chem. Soc., **80**, 4751 (1958).
14) M. Kofler, A. Langemann, R. Ruegg, U. Gloor, U. Schwieter, J. Wursch, O. Wiss, O. Isler : Helv. Chim. Acta, **42**, 2252 (1959).

It consisted of about 6 parts of dihydrodeoxytauranin (IIa) and 4 parts of *epi*-dihydrodeoxytauranin (IIb) (see below).

Repeated crystallization of the mixture from hexane yielded the minor component, *epi*-dihydrodeoxytauranin (IIb) in pure form, orange yellow needles, m.p. 160~180° (decomp.), UV λ_{max}^{EtOH} mμ (log ε): 267 (4.11), 4.20 (3.03), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3410 (OH), 1664, 1646, 1624, 893 (quinone), slight difference in finger-print region from the epimeric mixture, NMR: 0.73 (s a half of d $CHCH_3$), 0.83 (s $2CH_3$), 0.87 (s CH_3), 1.1~2.0 (m CH_2, CH), 2.05 (d J=1.7 c.p.s. ring CH_3), 2.2~2.5 (m CH_2 adjacent to quinone ring), 6.48 (q J=1.7 c.p.s. ring H), 6.98 (s OH), *Anal.* Calcd. for $C_{22}H_{32}O_3$: C, 76.70; H, 9.36. Found: C, 76.93; H, 9.25.

Dihydrodeoxytauranin Acetate (IIIa) and *epi*-Dihydrodeoxytauranin Acetate (IIIb)——A suspension of the epimeric dihydrodeoxytauranins (II) (50 mg.) and anhyd. sodium acetate (10 mg.) in Ac_2O (2 ml.) was heated on a water bath. The starting material was completely dissolved in 30 min. and the orange color changed to pale yellow. After cooling, the reaction mixture was poured into ice H_2O, and the resulting crystal-like precipitate was collected. It was dissolved in $CHCl_3$, passed through a column of silicic acid, and then crystallized from EtOH (40 mg.), m.p. 104~145°. It consisted of about 6 parts of dihydrodeoxytauranin acetate (IIIa) and 4 parts of the acetate of the *epi*-isomer (IIIb), as shown by comparison of the IR spectrum with that of artificial mixture of the two acetates in known composition. The mixture was separated by use of tweezers and by fractional crystallization from EtOH. From the more soluble fraction there was obtained dihydrodeoxytauranin acetate (IIIa) as yellow prisms, m.p. 119~120° and 135.5~136° (double melting), UV λ_{max}^{EtOH} mμ (log ε): 260 (4.18), 348 (2.78), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1787, 1171 ($OCOCH_3$), 1672, 1625 (quinone), NMR: (Fig. 1b) 0.83 (s $2CH_3$), 0.89 (s CH_3), 1.02 (s a half of d J=7 c.p.s. $CHCH_3$), 1.2~2.0 (m CH_2, CH), 2.04 (d J=1.5 c.p.s. ring CH_3), 2.33 (s $OCOCH_3$), 2.3~2.7 (m CH_2 adjacent to quinone ring), 6.58 (q J=1.5 c.p.s. ring H), *Anal.* Calcd. for $C_{24}H_{34}O_4$: C, 74.57; H, 8.87. Found: C, 74.88; H, 8.75.

The less soluble part afforded *epi*-dihydrodeoxytauranin acetate (IIIb), yellow plates, m.p. 158~159.5°, UV λ_{max}^{EtOH} mμ (log ε): 260 (4.09), 355 (2.82), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1788, 1176 ($OCOCH_3$), 1673, 1626 (quinone), NMR: (Fig. 1c) 0.72 (s a half of d J=4 c.p.s. $CHCH_3$), 0.81 (s CH_3), 0.83 (s CH_3), 0.87 (s CH_3), 1.0~1.9 (m CH_2, CH), 2.04 (d J=1.6 c.p.s. ring CH_3), 2.34 (s $OCOCH_3$), 2.2~2.5 (m CH_2 adjacent to quinone ring), 6.61 (q J=1.6 c.p.s. ring H), *Anal.* Calcd. for $C_{24}H_{34}O_4$: C, 74.57; H, 8.87. Found: C, 74.78; H, 8.65. *epi*-Dihydrodeoxytauranin (IIb) on acetylation gave a single product, *epi*-dihydrodeoxytauranin acetate (IIIb).

Dihydrodeoxytauranin Leucotriacetate (IV)——a) From the epimeric mixture of dihydrodeoxytauranins (II): A mixture of the dihydrodeoxytauranins (II) (100 mg.), anhyd. sodium acetate (20 mg.) and Zn powder (100 mg.) was suspended in Ac_2O (2 ml.) and heated on a water bath for 15 min., when the solution became colorless. The Zn was filtered off while hot, the filtrate treated with ice H_2O after cooling, and the resulting pasty precipitate was crystallized from EtOH (37 mg.); m.p. 119~122° after two more recrystallizations.

b) From dihydrodeoxytauranin acetate (IIIa): Dihydrodeoxytauranin acetate (50 mg.) was reductively acetylated by the same procedure described above to yield a crude crystalline product (57 mg.). Several recrystallizations from EtOH gave colorless fine needles, m.p. 123~124°, UV: λ_{max}^{EtOH} 267 mμ (log ε 2.65), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1781, 1200, 1190, 1178 ($OCOCH_3$), NMR: (at 100 mc.) 0.83 (s CH_3), 0.85 (s CH_3), 0.90 (s CH_3), 0.98 (d J=6.7 c.p.s. $CHCH_3$), 1.2~2.0 (m CH_2, CH), 2.15 (s arom. CH_3), 2.31 (s $OCOCH_3$), 2.33 (s $2OCOCH_3$), 2.3~2.8 (m benzylic CH_2), 6.85 (s arom. H), *Anal.* Calcd. for $C_{28}H_{40}O_6$: 71.16; H, 8.53. Found: C, 71.35; H, 8.43.

Dihydroxyquinone (VII)——A solution of *epi*-dihydrodeoxytauranin (IIb) (100 mg.) and an equimolecular amount of aniline in EtOH (4 ml.) was refluxed for 2.5 hr., when a dark violet anilino-derivative precipitated. The solvent was evaporated and to the crude product (114 mg.) there were added AcOH (15 ml.) and 60% aq. H_2SO_4 (0.8 ml.). The mixture was heated on a water bath for 1 hr., during which additional amounts of AcOH (5 ml.) and 60% H_2SO_4 (0.2 ml.) were added to dissolve the precipitate completely. After cooling, the yellow solution was poured into H_2O, and the resulting precipitate was collected (92 mg.) and crystallized from benzene. Several recrystallizations and sublimation (200° 15 mm. Hg) afforded the pure dihydroxyquinone (VII), reddish orange fine needles, m.p. 257~259°, UV λ_{max}^{EtOH} mμ (log ε): 298 (4.28), 445 (2.32), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3375 (OH), 1631 (quinone), ν_{max}^{KBr} cm^{-1}: 3335 (OH), 1611 (quinone), *Anal.* Calcd. for $C_{22}H_{32}O_4$: C, 73.30; H, 8.95. Found: C, 73.39; H, 8.76.

Dihydrotauranic Acids (IX) and Dihydrotauranic Acid (X)——The epimeric mixture of dihydrodeoxytauranins (II) (478 mg.) in $CHCl_3$ (30 ml.) was treated with a stream of ozonized oxygen at −20°, until the solution turned colorless. It required 50 min. The solvent was removed under reduced pressure at a room temperature and the ozonide was treated with boiling H_2O for 2 hr. The crude product thus obtained (374 mg.) was chromatographed on silicic acid; from the eluate with $CHCl_3$ was obtained the epimeric mixture of dihydrotauranic acids (IX) (75 mg.), which crystallized as colorless needles from CH_3CN, m.p. 108~109°, IR ν_{max}^{KBr} cm^{-1}: 3400~2400 (broad), 1705, 1418, 935 (acid), NMR: 0.79 (s a half of d $CHCH_3$), 0.82 (s CH_3), 0.86 (s $2CH_3$), 1.02 (s a half of d $CHCH_3$), 1.0~2.0 (m CH_2, CH), 2.0~2.7 (m $CHCH_2COO$), *Anal.* Calcd. for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 76.08; H, 10.89. Methyl

ester (prepared by reacting with diazomethane), IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1732, 1290, 1161 (ester). The unsaturated acid (XVI), m.p. 113~118.5°, which was derived from sclareol by Stoll and Hinder,[7] was hydrogenated to the saturated acid under the same conditions described in the literature. Two recrystallizations from hexane afforded colorless needles, m.p. 106~107.5°, undepressed upon admixture with dihydrotauranic acids (IX). The IR spectrum was superimposable with that of IX.

From the fraction eluted before dihydrotauranic acids (IX), another crystalline acid (X) was obtained (14 mg.), which was crystallized from CH_3CN, colorless plates, m.p. 113.5~114.5°, IR ν_{max}^{KBr} cm^{-1} : 3400~2400 (broad), 1711, 1416, 927 (acid).

Optical Rotatory Dispersion Measurements of the Acid (IX)——Only rough ORD measurements of the acid (IX), derived from tauranin and from the unsaturated acid (XVI), could be carried out because of the very limited amount. Both samples exhibited a plain negative curve with the following approximate values (in MeOH, at 14°) :

from tauranin (c=0.56) : $[\alpha]_{546}$ +8°; $[\alpha]_{306}$ 0°; $[\alpha]_{291}$ −73°
from XVI (c=0.47) : $[\alpha]_{546}$ +11°; $[\alpha]_{305}$ 0°; $[\alpha]_{291}$ −92°

Gas Chromatography of Methyl Esters of C_{16}-Acids——The three acids, IX from tauranin, IX from the unsaturated acid XVI, and X from tauranin, were methylated with Et_2O-CH_2N_2 and subjected to gas chromatography. The retention times are listed below.

	Retention time (min.)		Relative intensity
IX from tauranin	23.9	25.6	6:4
IX from XVI	23.7	25.4	6:4
X from tauranin	23.7	—	—

Hydroxy-γ-lactone (XVII)——Tauranin (989 mg.) was finely powdered and dissolved in 0.1*N* NaOH (200 ml.), to which there was added 30% aq. H_2O_2 (50 ml.); the violet color of the solution soon faded. After the reaction mixture was left standing for 1 hr. at a room temperature, it was acidified with 6*N* HCl, when a white precipitate was formed. It was taken up in Et_2O and divided into neutral (221 mg.) and acid (353 mg.) fractions in the usual way. The neutral part was further fractionated by chromatography on silicic acid, when a crystalline substance was obtained from the fraction eluted with $CHCl_3$ (37 mg.). Several recrystallizations from benzene afforded the hydroxy-γ-lactone (XVII) as colorless long prisms, m.p. 120.5~121°, IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 3635, 3420 (OH), 1768 (γ-lactone), NMR : 0.88 (s $3CH_3$), 1.0~2.3 (m CH_2, CH), 2.3~3.0 (m $CHCH_2CO$), 3.47 (broad s CH_2O), *Anal.* Calcd. for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84. Found : C, 72.57; H, 9.68.

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Summary

The structure of tauranin, a metabolic pigment from *Oospora aurantia*, has been established as shown by I. The relations of the three C_{16}-acids derived from ambrein, sclareol, and manool have been clarified.

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