Synthesis of Grifolin and Dihydrodeoxytauranin

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Condensation of farnesol and orcinol afforded grifolin (II; R = H). Grifolin diacetate was cyclised on treatment with boron trifluoride to a tricyclic compound (IV), having the same skeleton as tauranin (I). Compound (IV) was converted into dihydrodeoxytauranin acetate (IXa and b).

TAURANIN is a red pigment isolated from the mycelium of *Oospora aurantia* Sacc.[1] and has been shown to have structure (I).[2] This structure contains a bicyclic sesquiterpenoid group attached to substituted benzoquinone, and is thought to be derived biogenetically in a straightforward manner from a farnesyl pyrophosphate unit and the orcinol type condensate of an acetogenin.[2,3]

One of us (H. K.) studied an antibiotic substance, grifolin, isolated from the fungus *Grifola confluens*, and found it had the structure (II; R = H) in which a farnesyl group is attached to an orcinol group.[4] Thus, grifolin is considered to be an intermediate in the biosynthesis of tauranin from farnesyl pyrophosphate and orcinol (or orcenic acid[5]). This paper describes a biogenetic-type synthesis of grifolin from farnesol and orcinol, and the chemical transformation of grifolin into dihydrodeoxytauranin.

A biogenetic-type synthesis of a natural phenolic compound bearing an isoprenoid side chain was studied by Miller and Wood[6] in 1968, and they found that the reaction of 3,3-dimethylallyl diphenyl phosphate and phenol affords 2,2-dimethylchroman, which would be formed by cyclisation of the intermediate *o*-isopentenylphenol. Recently, Jurd and his co-workers[7] found that in dilute aqueous formic acid at room temperature 2-methylbut-3-en-2-ol reacts quite smoothly with hydroquinone to yield isopentenylhydroquinone without cyclisation. These condensation reactions seem to proceed by electrophilic substitution of the phenols by dimethylallyl cation produced from the phosphate of the allyl alcohol. Farnesol was expected to give an allyl cation corresponding to the side chain of grifolin and to react with phenol.[8]

Farnesol was warmed with orcinol in acetic acid, and the product gave a colourless oil. The n.m.r. spectrum of the compound indicated the presence of three methyl groups (δ 1·62 and 1·68) bonded to olefinic linkages, one methyl (δ 2·28) bonded to an aromatic ring and a methyl group (δ 1·14) bonded to a tertiary carbon atom. From these and the other physical properties, the structure of the condensation product was assigned as (III; R = H). This structure was confirmed by direct comparisons with isogrifolin which had been obtained by acid catalysed cyclisation of grifolin.[4]

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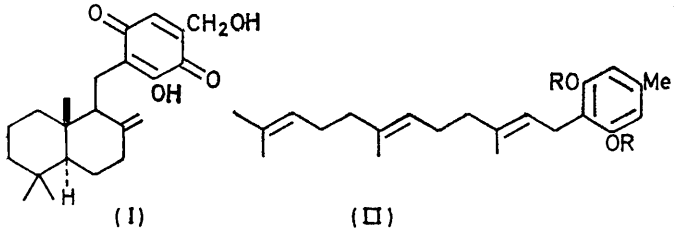
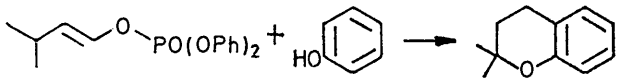
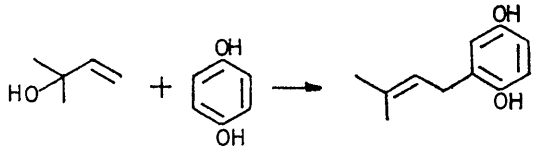
[2] K. Kawashima, K. Nakanishi, and H. Nishikawa, *Chem. Pharm. Bull.* (*Japan*), 1964, **12**, 796.
[3] R. W. Richards in ' Recent Development in the Chemistry of Natural Phenolic Compounds,' ed. W. D. Ollis, Pergamon, Oxford, 1961, p. 1.
[4] T. Goto, H. Kakisawa, and Y. Hirata, *Tetrahedron*, 1963, **19**, 2079.
[5] W. D. Ollis and I. O. Sutherland in ' Recent Developments in Chemistry of Natural Phenolic Compounds,' ed. W. D. Ollis, Pergamon, Oxford, 1961, p. 47; G. A. Ellestad, R. E. Evans, jun., and M. P. Kunstmann, *Tetrahedron*, 1969, **25**, 1323.
[6] J. A. Miller and H. C. S. Wood, *J. Chem. Soc.* (*C*), 1968, 1837.
[7] L. Jurd, K. Stevens, and G. Manners, *Tetrahedron Letters*, 1971, 2275.
[8] R. Mechoulam and B. Yagen, *Tetrahedron Letters*, 1969, 5349.

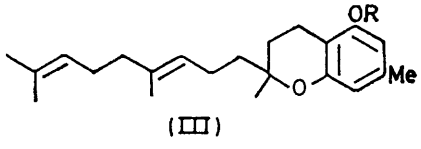
The condensation of farnesol and orcinol was conducted under sufficiently mild conditions to prevent the cyclisation of the farnesylorcinol (grifolin), in methylene



(I) (II)







(III)

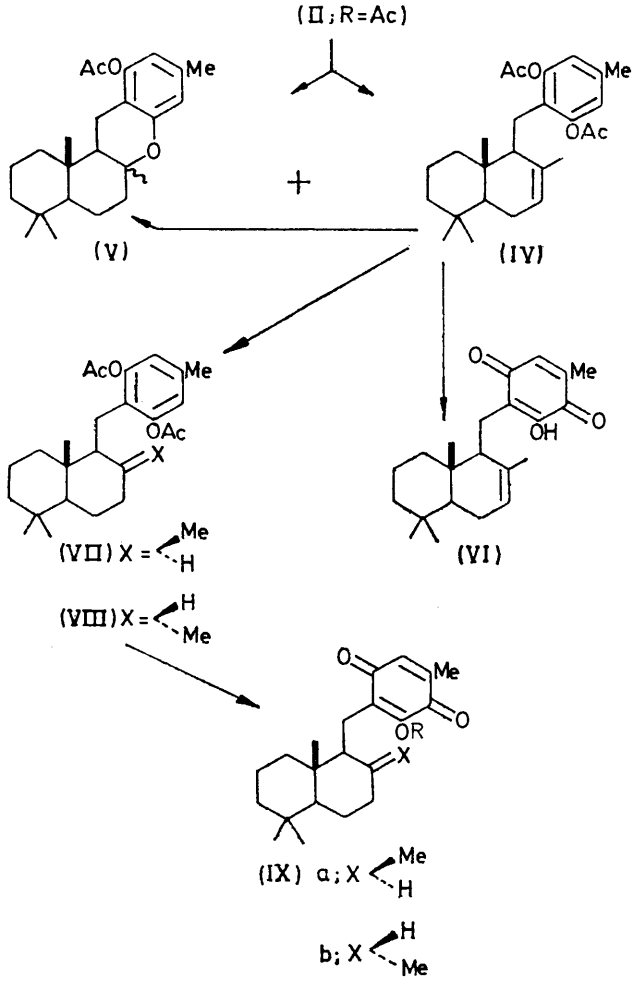
chloride in the presence of a trace of toluene-*p*-sulphonic acid at room temperature. The product was fractionated by silicic acid chromatography and the fractions giving a positive Gibbs test were collected to obtain an oil, which was identical with authentic grifolin.

The cyclisation of the triene residue of grifolin would construct the carbon skeleton of tauranin (I). These types of cyclisation of 1,5,9-trienes were studied extensively by Stork and Eschenmoser, and they found that acid catalysed cyclisation of a farnesic acid affords a *trans*-decalincarboxylic acid.[9] Treatment of grifolin diacetate (II; R = Ac) with boron trifluoride–ether gave a mixture of cyclised compounds, which were separated by chromatography on silicic acid and silver nitrate-impregnated silicic acid to obtain a tricyclic compound (IV) and a tetracyclic compound (V). The structure and stereochemistry of the tricyclic compound (IV) were assigned from its spectral properties and an assumption that the reaction proceeded *via* a stereoselectively concerted process. The stereochemistry was confirmed by converting (IV) into dihydrodeoxytauranin acetates (IXa and b; R = Ac).

The structure of the tetracyclic compound (V) was also assigned from its spectral properties; whereas the n.m.r. spectrum of the tricyclic compound (IV) showed a vinyl proton at δ 5·45 and an allyl methyl group at δ 1·55 as well as three tertiary methyl groups (at δ 0·85 and 0·90), the tetracyclic compound showed neither vinyl proton nor allyl methyl group, but showed four tertiary methyl groups at δ 0·85 (3H), 0·90 (6H), and 1·18 (3H), and one aryl methyl group at δ 2·23 This structure was confirmed by transformation of the tricyclic compound (IV) into the tetracyclic compound (V) by acid treatment.

Base catalysed hydrolysis of the tricyclic compound (IV) and subsequent oxidation of the resulting resorcinol with Fremy's salt[10] afforded a hydroxy-quinone (VI), the u.v. absorption of which was coincident with that of tauranin (I).

Catalytic hydrogenation of tricyclic compound (IV) in the presence of palladised charcoal afforded the dihydrocompounds as a mixture of epimers (VII) and (VIII) in a



ratio 1 : 1. The mixture was separated by repeated recrystallisation to yield (VII) as plates and (VIII) as fine needles. The n.m.r. spectra of these dihydrocompounds showed the secondary methyl signals at δ 0·96 (d, *J* 7·0 Hz) and 0·74 (d, *J* 5·5 Hz), respectively.

[9] G. Stork and A. W. Burgstahler, *J. Amer. Chem. Soc.*, 1955, **77**, 5068; P. A. Sttadler, A. Eschenmoser, H. Schnis, and G. Stork, *Helv. Chim. Acta*, 1957, **40**, 2191.

[10] H. J. Tauber, *Chem. Ber.*, 1953, **86**, 1495; O. Dann and H. G. Zeller, *ibid.*, 1960, **93**, 2829.

Acid catalysed hydrolysis of the dihydro-epimer (VII) and subsequent oxidation with Fremy's salt afforded a hydroxy-quinone (IXa; R = H). A monoacetate (IXa; R = Ac) derived from the hydroxy-quinone had identical spectral properties with the authentic dihydrodeoxytauranin acetate [2] (u.v., i.r., and n.m.r.). By the same reactions, the mixture of (VII) and (VIII) was converted into a mixture of quinone acetates, from which epimeric quinone acetate (IX; R = Ac) was obtained in the pure state. Spectral properties of the epimer (IXb; R = Ac) were coincident with the *epi*-dihydrodeoxytauranin acetate.[2]

The configuration at C-8 in the dihydro-compounds (VII) and (VIII), and in the quinone acetates (IXa and b), was assigned from their n.m.r. spectra. The aromatic group in four compounds (VII), (VIII), and (IXa and b; R = Ac), would not strongly affect the chemical shifts of C-8 methyl groups, because the chemical shifts of these groups were not changed on conversion of aromatic rings in (VII) (δ 0·98) and (VIII) (δ 0·74) into the quinones (IXa; R = Ac) (δ 0·98) and (IXb; R = Ac) (δ 0·77), respectively. The differences of the chemical shifts in each epimeric pair are attributable to steric effects.[11] The proximity of an axial methyl group at C-8 to the angular methyl group at C-10 would shift an axial methyl signal downfield compared with an equatorial methyl signal. Thus, the epimers (VII) and (IXa; R = Ac) have axial methyl groups, and the other epimers, (VIII) and (IXb; R = Ac), equatorial methyls. These assignments were compatible with the fact that splitting of a methyl group by the adjacent hydrogen is generally less for an equatorial methyl than for an axial methyl.[12] For the equatorial methyl compounds (VIII) and (IX; R = Ac), the coupling constant is 5·5 Hz, and for the axial compounds (VII) and (IXa; R = Ac), it is 7·0 Hz.

EXPERIMENTAL

M.p.s were determined in sealed capillary tubes. I.r. spectra were recorded on a Hitachi EPI-S-2 and u.v. spectra on a Hitachi EPS-3T spectrophotometer. N.m.r. spectra were measured on a Hitachi H-60 instrument using tetramethylsilane as an internal reference. Column chromatography was done with 100 mesh powder of silicic acid (Mallinckrodt), and silver nitrate impregnated silicic acid chromatography was carried out as described in literature.[13] The analytical t.l.c. plates were coated with a 1 mm thickness of E. Merck silica gel G.

Condensation of Orcinol and Farnesol.—(a) *Using acetic acid.* A solution of farnesol (2·2 g) and orcinol (1·6 g) in 50% acetic acid (10 ml) was heated on a water-bath for 6 h. The reaction mixture was poured into ice–water and extracted with ether. After removal of the solvent, the resultant oil (4·0 g) was chromatographed on silicic acid, and fractions with the same R_F value as grifolin and a positive Gibbs test were collected, to give an oil (215 mg), $\nu_{max.}$ (film) 3400, 2920, 1628, 1590, 1378, 1050, and 830 cm^{-1}, δ ($CDCl_3$) 1·14 (3H, s), 1·62 (6H, s), 1·68 (3H, s), 2·18 (3H, s), 3·35 (2H, d, *J* 7 Hz), 5·1 (3H, m), and 6·2 (2H, s). The crude oil (144 mg) was dissolved in dry pyridine (5 ml), and the solution was treated with *p*-nitrobenzoyl chloride (566 mg). The mixed solution was left overnight at room temperature, and the excess of acid chloride was decomposed by addition of ice–water. The solution was extracted with ether, and the ether extract was dried (Na_2SO_4). The solvent was removed to give an orange oil (195 mg), which was chromatographed on silicic acid to yield a colourless oil (83 mg), $\nu_{max.}$ (film) 3120, 2930, 1740, 1630, 1527, 1260, 870, 850, and 720 cm^{-1}, δ ($CDCl_3$) 1·26 (3H, s), 1·60 (6H, s), 1·65 (3H, s), 2·56br (2H, t), 5·1 (2H, m), 6·54 (1H, s), 6·56 (1H, s), and 8·32 (4H, s). The spectral properties were identical with those of isogrifolin *p*-nitrobenzoate (III; R = *p*-NO_2·C_6H_4·CO).

(b) *Using toluene-*p*-sulphonic acid.* A mixture of farnesol (220 mg), orcinol (160 mg), and a trace of toluene-*p*-sulphonic acid in methylene chloride (10 ml) was stirred at room temperature for 10 days. The resulting mixture was diluted with chloroform, washed with water, and dried (Na_2SO_4). Evaporation of the solvent afforded a crude oil (299 mg). The oil was purified by column chromatography on silicic acid, and fractions eluted with chloroform gave an oil (47 mg) with a positive Gibbs test. This was further purified through silicic acid column chromatography, and the fractions eluted with n-hexane–benzene (1 : 1) were collected to give an oil (24 mg), whose i.r. spectrum was identical with that of natural grifolin. Synthetic grifolin (24 mg) was treated with *p*-nitrobenzoyl chloride (65 mg) in dry pyridine (1·6 ml) at room temperature overnight. The mixture was poured into ice–water and extracted with ether. The ether layer was washed with water, dried (Na_2SO_4), and evaporated to give an oil (34 mg). This was purified by column chromatography on silicic acid (benzene elution) to give an oil (24 mg), with spectral properties (i.r. and n.m.r.) identical with authentic grifolin bis-*p*-nitrobenzoate derived from natural grifolin.

Acetylation of Grifolin (II; R = H).—Grifolin was acetylated using acetic anhydride and pyridine to give grifolin diacetate (II; R = Ac) (1·26 g), as an oil, $\nu_{max.}$ (film) 2930, 1765, 1625, 1575, 1365, 1192, and 1042 cm^{-1}, δ ($CDCl_3$) 1·58 (6H, s), 1·68 (3H, s), 1·70 (3H, s), 2·26 (6H, s, Ac), 2·30 (3H, s, *Me*Ar), 3·12 (2H, d, *J* 6·5 Hz), 5·65 (3H, m), and 6·75 (2H, s).

Cyclisation of Grifolin Diacetate (II; R = Ac).—To a stirred solution of grifolin diacetate (1·26 g) in dry benzene (20 ml) was added dropwise a solution of boron trifluoride–ether (11 ml) in dry benzene (120 ml) at below 5°, and the solution was stirred in a refrigerator for 72 h. The resulting solution was poured into ice–water and extracted with ether. The organic layer was washed well with water and dried (Na_2SO_4), and the ether was evaporated off to give a brown oil (1·26 g). Chromatography with silicic acid gave tetracyclic compound (V) as a colourless oil [elution with n-hexane–benzene (1 : 1)]. This oil was crystallised by addition of a few drops of ethanol and recrystallised from n-hexane to give 1,3,4,4a,5,6,6a,12,12a,12b-*decahydro*-4,4,6a,9,12b-*pentamethyl*-2H-*benzo*[a]*xanthen*-11-*yl acetate* (V) (10% yield), m.p. 118—119°, $\nu_{max.}$ (KBr) 2950, 1765, 1630, 1580, 1207, 1053, 882, and 826 cm^{-1}, δ ($CDCl_3$) 0·83 (3H, s), 0·88 (6H, s), 1·20 (3H, s), 2·20 (3H, s, Ac), 2·23br

[11] F. Johnson, N. A. Starkovsky, and G. Gurowiz, *J. Amer. Chem. Soc.*, 1965, **87**, 3492.

[12] T. M. Moynehan, K. Schofield, R. A. Y. Jones, and A. R. Katritzky, *J. Chem. Soc.*, 1962, 2637.

[13] T. Norin and L. Westfelt, *Acta Chem. Scand.*, 1963, **17**, 1828.

(3H, t, *Me*Ar), 6·38br (1H, s), 6·47br (1H, s) (Found: C, 77·7; H, 9·0. $C_{24}H_{34}O_3$ requires C, 77·8; H, 9·25%).

Further elution with the same solvent gave a mixture of the other cyclised compounds. Further chromatography of this mixture with silver nitrate impregnated silicic acid gave 5-*methyl*-2-(1,4,4a,5,6,7,8,8a-*octahydro*-2,5,5,8a-*tetramethyl*-1-*naphthylmethyl*)-m-*phenylene diacetate* (IV) as crystals (15% yield), m.p. 126—126·5°, $\lambda_{max.}$ (EtOH) 267·5 (log ε 2·26) and 275sh nm (2·55), $\nu_{max.}$ (KBr) 2940, 1768, 1628, 1570, 1360, 1206, 1040, and 887 cm^{-1}, δ ($CDCl_3$) 0·87 (3H, s), 0·89 (6H, s), 1·55 (3H, s, allylic Me), 2·29 (9H, s, 2 × Ac and ring Me), 2·48 (2H, m, benzylic methylene), 5·45 (1H, m olefinic proton), and 6·41 (2H, s) (Found: C, 75·8; H, 8·4. $C_{26}H_{36}O_4$ requires C, 75·7; H, 8·8%).

Conversion of Tricyclic Compound (IV) *into Tetracyclic Compound* (V).—A solution of tricyclic compound (IV) (33 mg) in 2N-ethanoic hydrochloric acid (10 ml) was heated to reflux for 4 h under nitrogen. After cooling, the solution was extracted with ether, and the extracts were dried (Na_2SO_4). Evaporation of the solvent gave an oil (36 mg), which was acetylated with acetic anhydride and pyridine without purification. The resulting product (33 mg) was chromatographed on silicic acid to give an oil (26 mg) which crystallised on treatment with ethanol. The spectra of this substance were in good agreement with those of authentic (V).

Conversion of Tricyclic Compound (IV) *into the Hydroxy-quinone* (VI).—To a solution of (IV) (60 mg) in ethanol (10 ml), was added a solution of potassium hydroxide (398 mg) in ethanol (20 ml), and the solution was heated to reflux for 4 h under nitrogen. After cooling, the solution was neutralised with 2N-hydrochloric acid (4 ml) and extracted with ether. After removal of the solvent, the residual oil was chromatographed on silicic acid. The fractions eluted with benzene–n-hexane (1 : 1) gave orange crystals (5 mg), which were identical with the hydroxy-quinone (VI). The fraction eluted with benzene gave an oil (30 mg), $\nu_{max.}$ (film) 3420, 2930, 1625, 1584, 1045, 815, and 755 cm^{-1}. The oily compound was oxidised without further purification. To a solution of the oil (340 mg) in acetone (8 ml), was added a mixed solution of Fremy's salt (105 mg) and dihydrogen potassium phosphate (105 mg), and the solution was stirred in a refrigerator for 70 h. From an ether extract of the reaction mixture, orange crystals were obtained, and were recrystallised from ethanol to give 3-*hydroxy*-5-*methyl*-2-(1,4,4a,5,6,7,8,8a-*octahydro*-2,5,5,8a-*tetramethyl*-1-*naphthylmethyl*)-p-*benzoquinone* (VI) (13 mg) as orange needles, m.p. 180—182°, $\lambda_{max.}$ (EtOH) 266 (log ε 4·14) and 416 nm (3·13), $\nu_{max.}$ (KBr) 3330, 2930, 1649, 1631, 1611, 1363, 1300, 1200, 1057, 980, and 896 cm^{-1} (Found: M^+, 342·220. $C_{22}H_{30}O_3$ requires 342·219).

Hydrogenation of Tricyclic Compound (IV).—The tricyclic compound (IV) (193 mg) in ethanol (20 ml) was hydrogenated over Pd–C (10%; 200 mg) and it absorbed 9 ml of hydrogen at room temperature after 24 h to yield an epimeric mixture of (VII) and (VIII) (180 mg) as crystals, m.p. 145°, $\nu_{max.}$ (KBr) 2950, 1765, 1625, 1575, 1360, 1186, 1040, 875, and 866 cm^{-1}, δ ($CDCl_3$) 0·74 [3H, d, *J* 5 Hz, *Me*CH of (VIII)], 0·83 (6H, s), 0·90 (3H, s), 1·03 [one half of doublet of *Me*CH of (VII)], 2·30 (9H, s, 2 × Ac and Ar*Me*), 2·45 (2H, m, benzylic methylene), and 6·69br (2H, s, ArH), δ (C_6H_6) 0·85 (6H, s), 0·86 [one half of doublet of *Me*CH of (VIII)], 0·94 (3H, s), and 1·04 [3H, d, *J* 7 Hz, *Me*CH of (VII)].

Repeated recrystallisation of the epimeric mixture from ethanol, and manual separation yielded 5-*methyl*-2-(2β,5,5,8a-*tetramethylperhydro*-1-*naphthylmethyl*)-m-*phenylene diacetate* (VII) as plates, m.p. 132—133°, $\nu_{max.}$ (KBr) 2940, 1760, 1630, 1575, 1365, 1200, 1185, 1170, 1055, and 1040 cm^{-1}, δ ($CDCl_3$) 1·02 (one half of doublet of *Me*CH), δ (C_6H_6) 1·04 (3H, d, *J* 7 Hz, *Me*CH) (Found: C, 75·4; H, 9·3. $C_{26}H_{38}O_4$ requires C, 75·3; H, 9·2%).

Conversion of Dihydro-compound (VII) *into Quinone Acetate* (IXa; R = Ac).—The pure dihydro-compound (VII) (30 mg) was hydrolysed in 2N-hydrochloric acid (6 ml) by refluxing for 4 h under nitrogen. The ether extract of the cooled reaction mixture gave crude crystals (28 mg) on evaporation of the solvent. The crude crystals were treated with Fremy's salt (108 mg) in 50% aqueous acetone (16 ml) in the presence of dihydrogen potassium phosphate (105 mg) as a buffer reagent for 44 h to obtain orange crystals, which were acetylated with acetic anhydride (2 ml) and sodium acetate (20 mg) by heating on a water-bath for 20 min. Recrystallisation of the acetylated product from ethanol gave 6-*methyl*-3-(2β,5,5,8a-*tetramethyl-perhydro*-1-*naphthylmethyl*)-p-*benzoquinonyl acetate* (IXa; R = Ac) (14 mg) as yellow needles, m.p. 138—139·5°, $\lambda_{max.}$ (EtOH) 260 (log ε 4·14) and 348 nm (2·38), $\nu_{max.}$ ($CHCl_3$) 2930, 1772, 1658, 1617, and 1170 cm^{-1}, δ ($CDCl_3$) 0·84 (3H, s), 0·86 (3H, s), 0·92 (3H, s), 0·98 (3H, d, *J* 7 Hz), 2·06 (3H, d, *J* 1·6 Hz), 2·35 (3H, s), 2·42—2·53 (2H, m), and 6·57 (1H, q, *J* 1·6 Hz), δ (C_6D_6) 1·05 (3H, d, *J* 7 Hz, *Me*CH). These spectral properties were identical with those of authentic dihydrodeoxytauranin acetate derived from natural tauranin.

Conversion of a Mixture of (VII) *and* (VIII) *into the Quinone Acetates* (IXa *and* b; R = Ac).—The dihydro-compounds (VII) and (VIII) (150 mg), were hydrolysed by refluxing in 2N-ethanolic hydrochloric acid (24 ml) for 4 h under nitrogen. After cooling, the product was extracted with ether, and the extracts were dried (Na_2SO_4). Evaporation of the solvent gave a brown oil, $\nu_{max.}$ (film) 3400, 2930, 1625, 1593, 1510, 1160, 1040, 990, and 820 cm^{-1}, δ ($CDCl_3$) 0·76 (one half of doublet of *Me*CH of one of the epimers), 0·85 (6H, s), 0·96 (3H, s), 1·09 (one half of doublet of *Me*CH of the other epimer), 2·18 (3H, s, Ar*Me*), 2·58 (2H, m, benzylic methylene), 4·9 (2H, m, 2 × OH), and 6·15br (2H, s, ArH). The oil was oxidised with Fremy's salt without purification; the oil was dissolved in acetone (50 ml) and cooled in an ice-bath, a mixed solution of Fremy's salt (536 mg) and dihydrogen potassium phosphate (200 mg) in water (50 ml) was added, and the resulting solution was stirred in a refrigerator for 50 h. The product was extracted with ether. Evaporation of the dried (Na_2SO_4) extract gave a crystalline residue, which was recrystallised from ethanol to give orange crystals (96 mg), m.p. 133—134° (decomp.), $\lambda_{max.}$ (EtOH) 266 (log ε 4·11) and 418 nm (3·16), $\nu_{max.}$ (KBr) 3330, 2930, 1650, 1630, and 1612 cm^{-1}; these spectral properties were essentially identical with those of authentic dihydrodeoxytauranin, but a slight difference in the fingerprint region was observed in the i.r. spectrum.

A suspension of the synthetic hydroxy-quinone (50 mg) and sodium acetate (100 mg) in acetic anhydride (2 ml) was heated on a water-bath for 30 min. After cooling, the product was poured into ice–water, and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and the solvent was removed to obtain a crystalline residue (60 mg). Repeated recrystallisations from ethanol and manual separation yielded yellow needles (20 mg), m.p. 138—139·5°, which were identical with synthetic

dihydrodeoxytauranin acetate (IXa; R = Ac), and yellow plates (20 mg) were isolated from the mother liquor, m.p. 129—132°, $\lambda_{max.}$ (EtOH) 260 (log ε 4·14) and 352 nm (2·46), $\nu_{max.}$ ($CHCl_3$) 2950, 1774, 1657, and 1178 cm^{-1}, δ ($CDCl_3$) 0·77 (3H, d, *J* 5·5 Hz, *Me*CH), 0·82 (3H, s), 0·85 (3H, s), 0·88 (3H, s), 2·05 (3H, d, *J* 1·7 Hz, Ar*Me*), 2·34 (3H, s, Ac), and 6·58 (1H, q, *J* 1·7 Hz, ArH); these spectral properties were in good agreement with those of *epi*-dihydrodeoxytauranin acetate (IXb; R = Ac).[2]

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