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ANTHOCYANIDINS AND RELATED COMPOUNDS—X

PEROXIDE OXIDATION PRODUCTS OF 3-ALKYLFLAVYLIUM SALTS

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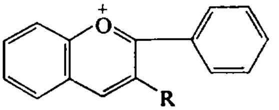
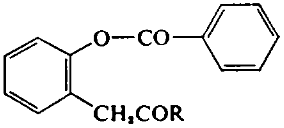
Abstract—In aqueous acetic acid solutions 3-alkylflavylium salts undergo a Baeyer-Villiger type oxidation with hydrogen peroxide to yield products formulated as 1-(2-hydroxyphenyl)-2-benzoyloxyprop-1-ene derivatives of type VIa. Under slightly alkaline conditions these oxidation products readily rearrange to *ortho*-benzoyloxybenzyl ketones, e.g. IXa. Alkaline hydrolysis of both VIa and IXa yields the desoxybenzoin VII. In aqueous methanolic solutions these flavylium salts undergo a different type of oxidation, resulting in the formation of 3-acyl-2-phenylbenzofurans.

IT HAS been reported that 3-phenylflavylium salts are oxidized by hydrogen peroxide[1] or ozone[2] in acetic acid solutions to *ortho*-benzoyloxydesoxybenzoins (Ia → IIa). 3-Methoxyflavylium salts[1] and natural anthocyanidin 3-glycosides[3] are oxidized similarly to *ortho*-benzoyloxyphenylacetic acid esters (Ib → IIb). In aqueous methanolic solutions, on the other hand, it was recently demonstrated[4] that peroxide oxidation of 3-methyl- and 3-methoxyflavylium salts primarily yields 3-acetyl- and 3-carbomethoxy-2-phenylbenzofurans respectively, e.g. IIIa → IVa, this oxidation proving a convenient synthetic route to coumestrol,[5] trifoliol[6] and other natural coumarinobenzofurans. From these different observations it is apparent that solvent variations may markedly effect flavylium salt oxidation reactions. A number of 3-alkylflavylium salts have now been oxidized both in aqueous methanol and aqueous acetic acid solutions and it has been confirmed that 3-acetyl-2-phenylbenzofurans are formed only in the alcoholic media. In the absence of methanol (or ethanol) a new type of oxidation product, *viz.*, an enol benzoate of structure VI, is formed.


Ia, R = C_6H_5-
Ib, R = OMe, OGl


IIa, R = C_6H_5-
IIb, R = OMe, OGl

Thus, peroxide oxidation of 3-methyl-4′-hydroxy-8-methoxyflavylium chloride IIIa in acidic or neutral aqueous methanol solutions yields the known[4] 3-acetyl-2-phenylbenzofuran IVa, $C_{17}H_{14}O_4$. In slightly alkaline, aqueous methanol solutions

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[1] W. Dilthey and W. Hoschen, *J. Prakt. Chem.* **246**, 42 (1933).

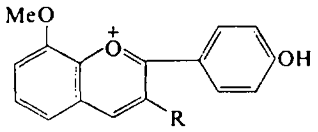
[2] R. L. Shriner and R. B. Moffett, *J. Amer. Chem. Soc.* **62**, 2711 (1940).

[3] P. Karrer, R. Widmer, A. Helfenstein, W. Hurliman, O. Nievergelt and P. Monsarrat-Thoms, *Helv. Chim. Acta* **10**, 729 (1927).

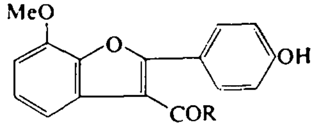
[4] L. Jurd, *J. Org. Chem.* **29**, 2602 (1964).

[5] L. Jurd, *J. Org. Chem.* **29**, 3036 (1964).

[6] A. L. Livingston, E. M. Bickoff, R. E. Lundin and L. Jurd, *Tetrahedron* **20**, 1963 (1964).

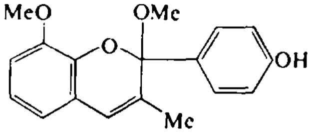


IIIa, R = Me
IIIb, R = Et



IVa, R = Me
IVb, R = Et

IIIa is converted primarily into the crystalline carbinol base methyl ether V, which is inert to oxidation under these conditions. Hydrogen peroxide oxidation of IIIa in aqueous acetic acid or, better, in aqueous acetic acid–sulfuric acid solutions, however, results in rapid crystallization of a colorless product, $C_{17}H_{16}O_5$. Chromatographic examination of these acetic acid reaction filtrates did not reveal the presence of even trace amounts of the benzofuran (IVa) although addition of small quantities (10%) of methanol to the aqueous acetic acid oxidation mixtures resulted in simultaneous formation of both the new product and the benzofuran. 3-Ethyl-4′-hydroxy-8-methoxyflavylium chloride (IIIb) is oxidized similarly to the 3-propionylbenzofuran (IVb) in aqueous methanol solutions and to a different, highly crystalline product, $C_{18}H_{18}O_5$, in aqueous acetic acid solutions.



V

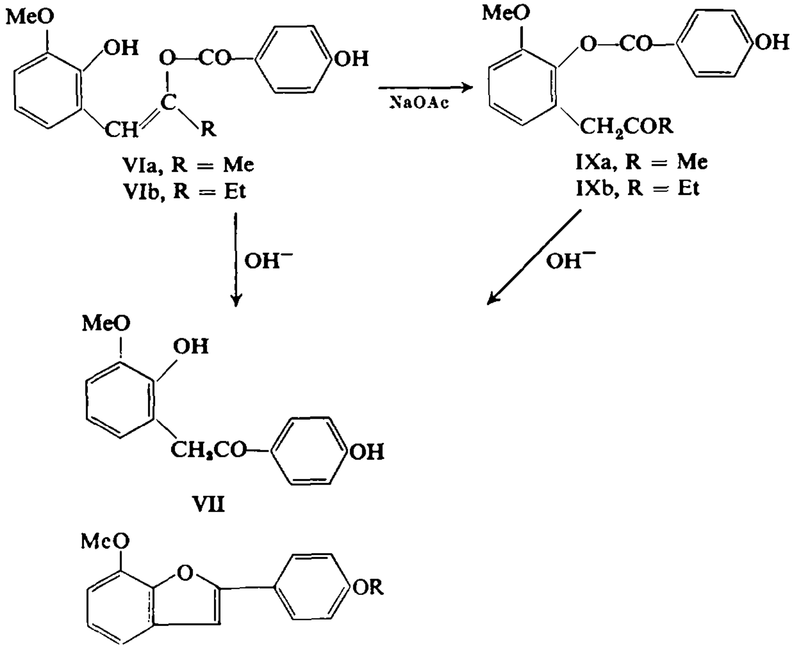
The $C_{17}H_{16}O_5$ and $C_{18}H_{18}O_5$ oxidation products form diacetyl and dibenzoyl derivatives and give intense blue colors with Gibbs reagent, indicating the presence of two free hydroxyl groups and, furthermore, that one of these hydroxyl groups is derived from the oxygen atom of the flavylium heterocyclic ring. The UV spectrum of each of the oxidation products in ethanol (λ_{max} 257 mμ, log ε 4·38) undergoes a pronounced bathochromic shift to λ_{max} 309 mμ (log ε 4·50) on the addition of sodium ethylate (Fig. 1). The magnitude of this alkali shift clearly indicates the second hydroxyl group is present in a 4-hydroxybenzoyl grouping.[7]

Acetyl analyses (by alkaline hydrolysis) on the C_{17} oxidation product showed the liberation of one equivalent of acetic acid and, therefore, *indicated* the presence of an acetyl group in the oxidation product. Acetyl analyses on the diacetate of the oxidation product similarly indicated the presence of three acetyl groups in this derivative. Dissolved in cold, aqueous alkali the C_{17} oxidation product rapidly hydrolyzed to yield a dihydroxy compound, $C_{15}H_{14}O_4$, the same C_{15} compound being obtained by alkaline hydrolysis of the C_{18} oxidation product. This hydrolysis product gave a positive Gibbs test and its NMR spectrum (in deuteroacetone) showed the presence of a methylene group (singlet, δ 4·22), a methoxyl group (singlet, δ 3·81), hydroxyl groups (multiplet, δ 3·60) and seven aromatic protons. Its λ_{max} in ethanol (280 mμ) shifted 50 mμ to λ_{max} 330 mμ in alcoholic sodium ethylate, indicative of the presence of a 4-hydroxyphenacyl grouping.[8] The C_{15} hydrolysis product was easily dehydrated

[7] Methyl 4-hydroxybenzoate has λ_{max} 257 mμ (log ε 4·21) in EtOH and λ_{max} 302 mμ (log ε 4·41) in ethanolic EtONa.

[8] 4-Hydroxyacetophenone has λ_{max} 278 mμ in EtOH and λ_{max} 328 mμ in ethanolic EtONa.

by mineral acids to yield a monohydroxy compound, $C_{15}H_{12}O_3$, the UV spectrum of which (λ_{max} 308, 300 mμ, log ε 4·54, 4·54) suggested the 2-phenylbenzofuran structure VIIIa. This was confirmed by methylation to yield a monomethyl derivative identical with the previously described[4] 2-(4-methoxyphenyl)-7-methoxybenzofuran (VIIIb). Thus, the C_{15} hydrolysis product is the desoxybenzoin (VII).



VIa, R = Me
VIb, R = Et

IXa, R = Me
IXb, R = Et

VII

VIIIa, R = H
VIIIb, R = Me

Acidification of the alcoholic sodium ethylate spectral solutions of the C_{17} and C_{18} oxidation products did not regenerate the original oxidation products but resulted in the formation of isomers with λ_{max} 262 mμ (Fig. 1c). The C_{17} oxidation product (m.p. 162–164°) quantitatively rearranged to its crystalline isomer (m.p. 126°) when briefly warmed with alcoholic sodium acetate. The C_{18} oxidation product (m.p. 150°) rearranged similarly to an isomer (m.p. 114°). As in the case of the oxidation products, alkaline hydrolysis of these isomers gave the desoxybenzoin (VII). These rearrangement products did not react with Gibbs reagent nor form colored complexes with ferric salts. They formed monoacyl and monoalkyl derivatives[*] and thus contained only one free hydroxyl group (present as a 4-hydroxybenzoyl grouping). The IR spectrum (KBr pellet) of the C_{18} isomer showed two intense bands at 1710 cm^{-1} and 1727 cm^{-1} (ester and ketonic carbonyl groups), the presence of the ketonic carbonyl group being further indicated by the formation of a monoxime. From these data the C_{17} and C_{18} rearrangement products are clearly the *ortho*-benzoyloxybenzyl ketones IXa and IXb respectively. In agreement with structure IXa the NMR spectrum of the C_{17} isomer (in $CDCl_3$) showed a benzylic methylene group (as a singlet, δ 3·66) and an acetyl methyl (as a singlet, δ 2·13).

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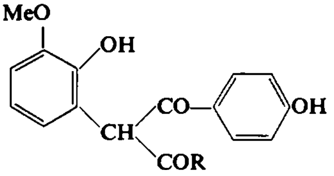
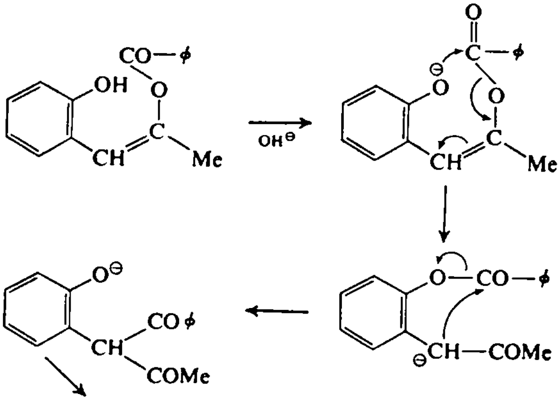
[*] Benzylation of the C_{17} and C_{18} oxidation products causes rearrangement with the formation of the monobenzyl derivatives of the isomeric compounds.

The C_{17} and C_{18} oxidation products form reddish-brown complexes with alcoholic ferric chloride. β-Diketones characteristically form red-brown ferric complexes and hydrolyze easily in alkaline solutions. The ferric reaction, acetyl analysis, ease of rearrangement and of hydrolysis of the oxidation products, therefore, suggest structures Xa and Xb for these compounds. These structures, however, have been excluded on the basis of further chemical and spectral considerations. Thus, if the red ferric reaction of the oxidation products is due to the presence of a β-diketone grouping, then the diacetyl and dibenzoyl derivatives of the oxidation products should also form red ferric complexes and, furthermore, should readily yield C- or O-alkyl derivatives. The acyl derivatives, however do not react with ferric salts nor with alkylating agents under mild conditions.[10] The oxidation products do not react with 2,4-dinitrophenylhydrazine hydrochloride and the IR spectrum of the C_{18} oxidation product in chloroform showed a *single* carbonyl band at 1717 cm^{-1} (attributed to an ester carbonyl). The NMR spectrum of the diacetate of the C_{17} oxidation product (Fig. 2) clearly shows the presence of a vinyl methyl group (doublet at δ 2·2, J = 1·0 c/s) and of a vinyl hydrogen (apparent quartet at δ 6·03, J = 1·0 c/s). These data are in complete accord with structures VIa and VIb for the oxidation products.



Xa, R = Me
Xb, R = Et

On the basis of structures VIa and VIb the ferric reactions of the oxidation products must arise from the guaiacyl nucleus, and in this connection it is noteworthy that the desoxybenzoin VII also forms a red-brown complex with ferric salts. The acetyl analysis and ease of hydrolysis of VIa is readily explained as proceeding through the isomer IXa and the ionized β-diketone Xa:



VII + AcOH

IX

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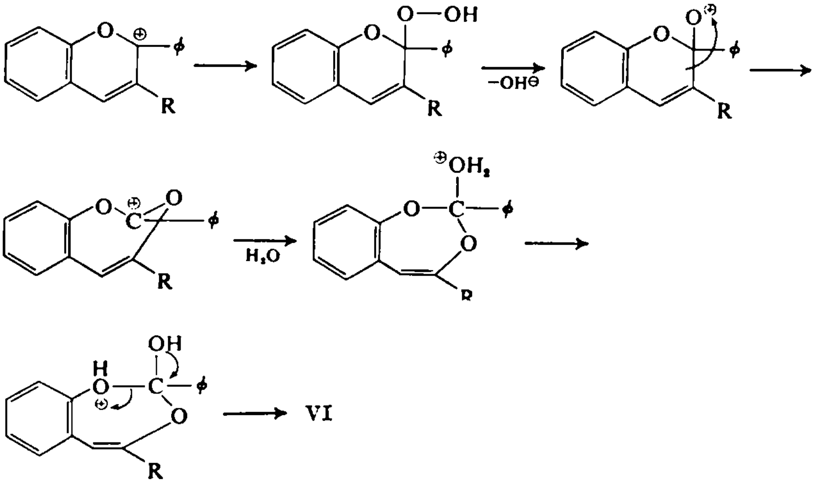
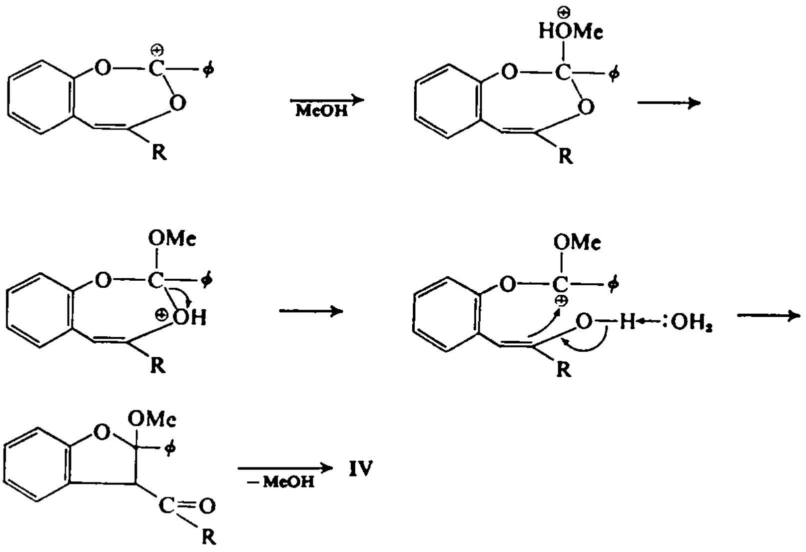
[10] Benzyl chloride and potassium carbonate in acetone solutions. Under these conditions 5,5-dimethyl-1,3-cyclohexanedione yields 2,2-dibenzyl-5,5-dimethyl-1,3-cyclohexanedione.

The oxidation of the flavylium salt IIIa to VIa in aqueous acetic acid solutions resembles the Baeyer-Villiger oxidation of ketones to esters. A similar reaction mechanism is plausible:[11]



Since the nucleophilicity of methanol greatly exceeds that of water, nucleophilic attack of methanol on the carbonium ion may compete with the above reaction in aqueous methanol solutions to yield 3-acetyl-2-phenylbenzofurans:[12]



A variety of phenolic 3-methyl- and 3-ethyl-flavylium salts have been oxidized in acetic acid solutions as described for IIIa and IIIb. In all of these cases, however, the products, presumably enol benzoates of type VI, did not crystallize.

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[11] Kindly suggested by T. A. Geissman, personal communication.

[12] The enol benzoate VIb has been detected as a minor product in the oxidation of IIIb to IVb in aqueous ethanol solutions.

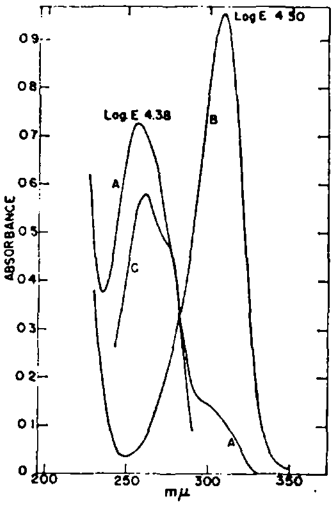

FIG. 1. UV spectrum in EtOH of (A) VIb (c = 3·01 × 10^{-5} m/l.), (B) VIb + EtONa, (C) IXb.

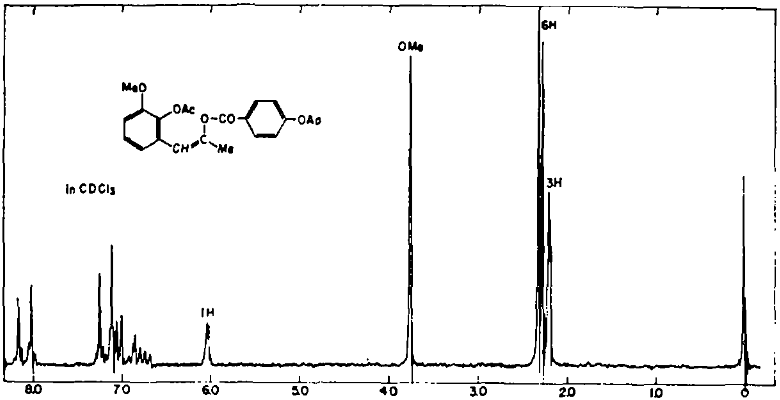

FIG. 2. 60 Mc NMR spectrum of VIa diacetate in $CDCl_3$; TMS as internal reference.

EXPERIMENTAL

3-*Ethyl-4′-hydroxy-8-methoxyflavylium chloride* (IIIb)

A solution of *o*-vanillin (60·0 g) and 4-hydroxybutyrophenone (60·0 g) in AcOEt (400 ml) and EtOH (100 ml) was saturated with HCl gas and allowed to stand for 24 hr. The crystalline flavylium salt was collected, washed in AcOEt and Et_2O and air-dried (81·0 g). A solution of this product (50·0 g) in boiling 10% HClaq (200 ml) and water (500 ml) was treated with norite, filtered and diluted with conc HCl (100 ml). The pure flavylium chloride separated as orange-red needles, m.p. 131–132°.

3-*Ethyl-4′-hydroxy-8-methoxyflavylium perchlorate*, prepared by adding 5% aqueous perchloric acid to a solution of the chloride in AcOH, separated as yellow prisms, m.p. 254–255°. (Found: C, 56·8; H, 4·68. Calc. for $C_{18}H_{17}O_7Cl$: C, 56·8; H, 4·50%.)

2-(4-*Hydroxyphenyl*)-3-*propionyl-7-methoxybenzofuran* (IVb)

30% H_2O_2 (10·0 ml) was added to a solution of IIIb (6·0 g) in MeOH (60·0 ml) and 20% H_2SO_4aq (30·0 ml) at room temp. Cream-colored crystals rapidly separated. After 10 min, water (30·0 ml) was added and the product was collected. Recrystallized from MeOH IVb was obtained as long, cream-colored needles, m.p. 150–151° (3·05 g); $\lambda_{\max}^{\mathrm{EtOH}}$ 312 (4·14) mμ (log ε), $\lambda_{\max}^{\mathrm{NaOEt}}$ 365 (4·22), 276, 253 mμ (log ε). (Found: C, 73·0; H, 5·54. Calc. for $C_{18}H_{16}O_4$: C, 73·0; H, 5·44%.)

Acetylation of the above product gave 2-(*4-acetoxyphenyl*)-*3-propionyl-7-methoxybenzofuran* as colorless needles (Ex. MeOH), m.p. 89°, $\lambda_{\max}^{\mathrm{EtOH}}$ 302, 251 mμ. (Found: C, 71·0; H, 5·39. Calc. for $C_{20}H_{18}O_5$: C, 71·0; H, 5·36%.)

The *monomethyl derivative of* IVb crystallized from MeOH as colorless needles, m.p. 72°, $\lambda_{\max}^{\mathrm{EtOH}}$ 310 mμ. (Found: C, 73·7; H, 5·86. Calc. for $C_{19}H_{18}O_4$: C, 73·5; H, 5·84%.)

1-(*2-Hydroxy-3-methoxyphenyl*)-*2-*(*4-hydroxybenzoyloxy*)-*but*-1-*ene* (VIb)

30% H_2O_2 (20·0 ml) was added to a solution of 3-ethyl-4′-hydroxy-8-methoxyflavylium chloride (10·0 g) in glacial AcOH (50·0 ml) and 10% H_2SO_4aq (100·0 ml) at 40–45°. The mixture became cloudy at once and was cleared by addition of more AcOH (50·0 ml). Within 1 or 2 min a mass of cream-colored crystals separated. After 30 min water (50 ml) was added and the product was collected. Recrystallized from MeOH containing 2 drops H_2SO_4, the product separated as colorless needles, m.p. 147–150° (4·21 g). Recrystallized twice from AcOHaq VIb was obtained as colorless prismatic needles or felted needles, m.p. 150°, $\lambda_{\max}^{\mathrm{EtOH}}$ 257 mμ (log ε 4·38), shoulder at 302 mμ, $\lambda_{\max}^{\mathrm{NaOEt}}$ 309 mμ (log ε 4·50). On silicic acid TLC the product migrates as a single species (R_F 0·29 in ether, 0·08 in ether-Skellysolve F, 2:1). (Found: C, 68·9; H, 5·77; MeO—, 10·0. Calc. for $C_{18}H_{18}O_5$: C, 68·9; H, 5·77; 1 MeO—, 9·87%.)

The *diacetate* of VIb, prepared by heating it (0·35 g) with Ac_2O (1·0 ml) and pyridine (5 drops) for 2 min, crystallized from aqueous MeOH as colorless needles, m.p. 84–85°, $\lambda_{\max}^{\mathrm{EtOH}}$ 239 mμ. (Found: C, 66·5; H, 5·57. Calc. for $C_{22}H_{22}O_7$: C, 66·3; H, 5·57%.)

The oxidation product VIb (0·5 g) was warmed with pyridine (3·0 ml) and benzoyl chloride (2·0 ml) for 5 min and diluted with water. The dibenzoate of VIb crystallized from acetone–MeOH as colorless, glistening plates, m.p. 121–122°. (Found: C, 73·6; H, 5·13. Calc. for $C_{32}H_{26}O_7$: C, 73·6; H, 5·02%.)

1-(2-(*4-Hydroxybenzoyloxy*)-*3-methoxy*)*phenylbutan-2-one* (IXb)

Compound VIb (2·0 g) was heated on a steam-bath with anhydrous AcONa (2·0 g) and abs. EtOH (20·0 ml) for 5 min. Water (100 ml) was added. The solid product was crystallized from aqueous MeOH; IXb separated as colorless, thick needles, m.p. 114° (1·61 g), $\lambda_{\max}^{\mathrm{EtOH}}$ 262 mμ (log ε 4·32), $\lambda_{\max}^{\mathrm{NaOEt}}$ 309 mμ (log ε 4·54). (Found: C, 68·8; H, 5·90; MeO—, 10·1. Calc. for $C_{18}H_{18}O_5$: C, 68·9; H, 5·77; 1 MeO—, 9·87%.)

The *acetate* of IXb crystallized from MeOH as colorless needles, m.p. 100°, $\lambda_{\max}^{\mathrm{EtOH}}$ 238 mμ, shoulders at 279 and 270 mμ. (Found: C, 67·6; H, 5·75; MeO—, 8·78; CH_3CO—, 23·5. Calc. for $C_{20}H_{20}O_6$: C, 67·4; H, 5·66; 1 MeO—, 8·71; 2 CH_3CO—, 24·1%.)

The *benzoate* of IXb separated from MeOH as long, colorless needles, m.p. 90–91°, $\lambda_{\max}^{\mathrm{EtOH}}$ 241 mμ, shoulders at 275 mμ. (Found: C, 71·8; H, 5·35. Calc. for $C_{25}H_{22}O_6$: C, 71·8; H, 5·30%.)

Compound IXb (0·20 g), AcONa (0·5 g) and hydroxylamine HCl (0·5 g) were dissolved in warm EtOH (5·0 ml) and water (10·0 ml). The hot solution was allowed to cool slowly and diluted with water (20 ml). The oily product crystallized on standing the mixture at 0°. Recrystallized from aqueous MeOH the *oxime* of IXb was obtained as colorless, granular crystals, m.p. 148–150°. (Found: C, 65·7; H, 5·79. Calc. for $C_{18}H_{19}O_5N$: C, 65·6; H, 5·82%.)

Compound IXb (0·2 g) was heated under reflux with benzyl chloride (1·5 ml), KI (0·5 g), K_2CO_3 (3·0 g) and acetone (20·0 ml) for 2 hr. The filtered acetone solution was concentrated, diluted with Skellysolve F and cooled. The oily product thereby crystallized. Recrystallized from MeOH the *benzyl ether of* IXb separated as colorless, glistening needles, m.p. 93°, $\lambda_{\max}^{\mathrm{EtOH}}$ 261 mμ. The benzyl ether of IXb, m.p. and m.m.p. 93°, was also obtained by benzylation of VIb under identical conditions. (Found: C, 74·2; H, 6·04; MeO—, 7·81. Calc. for $C_{25}H_{24}O_5$: C, 74·2; H, 5·98; 1 MeO—, 7·67%.)

2-(*4-Hydroxyphenyl*)-*3-acetyl-7-methoxybenzofuran* (IVa)

Oxidation of IIIa in aqueous MeOH as previously described[4] or in methanolic H_2SO_4aq gave IVa, m.p. 222°.

1-(2-*Hydroxy-3-methoxyphenyl*)2-(4-*hydroxybenzoyloxy*)prop-1-*ene* VIa

30% H_2O_2 (20·0 ml) was added to a solution of IIIa (10·0 g) in glacial AcOH (100·0 ml) and 10% H_2SO_4aq (100 ml) at 40°. After 30 min water (100 ml) was added and the crystalline product was collected. Recrystallized from aqueous AcOH VIa was obtained as colorless needles, m.p. 162–164° (dried *in vacuo* at 80°), $\lambda_{\max}^{\mathrm{EtOH}}$ 257 mμ (log ε 4·38), shoulder at 305 mμ, $\lambda_{\max}^{\mathrm{NaOEt}}$ 309 mμ (log ε 4·52) (3·1 g). With alcoholic $FeCl_3$ VIa gave an intense red-brown color. With Gibbs reagent it formed an immediate dark blue solution ($\lambda_{\max}$ 620 mμ). (Found: C, 68·0; H, 5·30; MeO—, 10·8; CH_3CO—, 13·8. Calc. for $C_{17}H_{16}O_5$: C, 68·0; H, 5·37; 1 MeO—, 10·3; 1 CH_3CO—, 14·3%.)

Warmed with Ac_2O and AcONa or with Ac_2O and pyridine VIa formed a *diacetyl derivative* which crystallized from aqueous MeOH as colorless, glistening needles, m.p. 123–124°, $\lambda_{\max}^{\mathrm{EtOH}}$ 239 mμ. (Found: C, 65·6; H, 5·24; 1 MeO—, 8·40; CH_3CO—, 32·9. Calc. for $C_{21}H_{20}O_7$: C, 65·6; H, 5·24; 1 MeO—, 8·07; 3 CH_3CO—, 33·6%.)

Benzoylation of VIa gave a *dibenzoate*, which crystallized from acetone–MeOH as colorless needles, m.p. 122–123°, $\lambda_{\max}^{\mathrm{EtOH}}$ 236 mμ. (Found: C, 73·3; H, 4·68; MeO—, 6·40. Calc. for $C_{31}H_{24}O_7$: C, 73·2; H, 4·76; 1 MeO—, 6·09%.)

1-(2-(4-*Hydroxybenzoyloxy*)3-*methoxy*)*phenyl-propan-2-one* (IXa)

Heated with alcoholic AcONa as described above, VIa rearranged to IXa, which crystallized from aqueous MeOH as colorless needles, m.p. 126°, $\lambda_{\max}^{\mathrm{EtOH}}$ 262 mμ (log ε 4·28), $\lambda_{\max}^{\mathrm{NaOEt}}$ 309 mμ (log ε 4·52). (Found: C, 68·0; H, 5·40. Calc. for $C_{17}H_{16}O_5$: C, 68·0; H, 5·37%.)

Acetylation of IXa gave a *monoacetate*, colorless needles (Ex. MeOH), m.p. 90°. (Found: C, 66·5; H, 5·38. Calc. for $C_{19}H_{18}O_6$: C, 66·7; H, 5·30%.)

2′,4-*Dihydroxy-3′-methoxdesoxybenzoin* (VII)

(a) The oxidation product VIa (2·0 g) or VIb (2·0 g) was dissolved in 10% NaOHaq (20·0 ml) at room temp and allowed to stand for 10 min. The solution was acidified with 10% HClaq (30 ml) and diluted with water (100 ml). The solid product was collected and crystallized from MeOH; VII was obtained as cream-colored, glistening plates which sinter at 151–152° and slowly melt up to 160°. This behavior may be due to partial dehydration to VIIIa; $\lambda_{\max}^{\mathrm{EtOH}}$ 280 mμ (log ε 4·27), $\lambda_{\max}^{\mathrm{NaOEt}}$ 330 mμ (log ε 4·41). On silicic acid TLC VII migrates as a single species (R_F 0·70 in Et_2O, 0·25 in ether-Skellysolve F, 2:1, and 0·26 in acetone–$CHCl_3$, 1:10). It gives a strong red-brown color with alcoholic $FeCl_3$.

Warmed with pyridine (1·0 ml) and benzoyl chloride (0·6 ml), VII (0·1 g) formed a *dibenzoate*. This crystallized from acetone–MeOH as colorless, glistening prisms, m.p. 138–139°, $\lambda_{\max}^{\mathrm{EtOH}}$ 235 mμ. (Found: C, 74·7; H, 4·73. Calc. for $C_{29}H_{22}O_6$: C, 74·7; H, 4·75%.)

(b) Compound IXa (2·0 g), hydrolyzed in 10% NaOHaq (10·0 ml) as described in (a), gave VII, m.p. and m.m.p. 150–160°; dibenzoate, m.p. and m.m.p. 138–139°.

2-(4-*Hydroxyphenyl*) 7-*methoxybenzofuran* (VIIIa)

20% H_2SO_4aq (5·0 ml) was slowly added to a boiling solution of VII (0·5 g) in glacial AcOH (5·0 ml). On allowing to cool, colorless crystals separated. Recrystallized from aqueous MeOH VIIIa was obtained as colorless needles, m.p. 124–125° (0·32 g), $\lambda_{\max}^{\mathrm{EtOH}}$ 308 (4·54), 300 (4·54), 250 (4·02) mμ (log ε), $\lambda_{\max}^{\mathrm{NaOEt}}$ 328 (4·60) mμ (log ε). (Found: C, 75·1; H, 5·11. Calc. for $C_{15}H_{12}O_3$: C, 75·0; H, 5·03%.)

Compound VIIIa was methylated with MeI, K_2CO_3 and acetone. The product crystallized from MeOH as colorless plates, $\lambda_{\max}^{\mathrm{EtOH}}$ 207 (4·49), 300 (4·49), 250 (3·87) mμ (log ε), m.p. and m.m.p. with authentic[4] VIIIb, 82°. Cochromatographed with authentic VIIIb on silicic acid, the methyl ether migrated as a single, blue fluorescent spot, R_F 0·84 in ether-Skellysolve F, 2:1, 0·78 in AcOEt–Skellysolve F, 1:4. (Found: C, 75·4; H, 5·61. Calc. for $C_{16}H_{14}O_3$: C, 75·6; H, 5·55%.)

3-*Methyl-4′-hydroxy-2,8-dimethoxyflav-3-ene* (V)

(a) A solution of IIIa (2·0 g) in MeOH (20·0 ml) and water (20·0 ml) was warmed for 5 min and allowed to cool. The colorless crystals which separated were recrystallized from aqueous MeOH; V was obtained as colorless needles which rapidly became pink on exposure to air. Heated it becomes red at about 115° and melts to a deep red liquid at 138–140°; $\lambda_{\max}^{\mathrm{EtOH}}$ 274 (4·11), 263 (4·13) mμ (log ε).

Warmed briefly with AcOH-10% HClaq V quantitatively regenerates IIIa. (Found: C, 72·6; H, 6·03; MeO—, 20·1. Calc. for $C_{18}H_{18}O_4$: C, 72·5; H, 6·08; 2 MeO—, 20·8%.)

The *acetate* of V crystallized from wet MeOH as colorless prisms, m.p. 101–102°, λ_{max}^{EtOH} 273 (4·02), 264 (4·05) mμ (log ε). (Found: C, 70·5; H, 5·93; MeO—, 18·4; CH_3CO—, 12·8. Calc. for $C_{20}H_{20}O_5$: C, 70·6; H, 5·92; 2 MeO—, 18·2; 1 CH_3CO—, 12·6%.)

(b) 30% H_2O_2 (4·0 ml) was added to a suspension of IIIa (2·0 g) in warm MeOH (20·0 ml) and sat $NaHCO_3$aq (20·0 ml). Rapid decoloration and precipitation of a colorless product occurred. Recrystallized from aqueous MeOH, V, m.p. and m.m.p. 138–140°, was obtained; *acetate*, m.p. and m.m.p. 101–102°.

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