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Synthesis of Ripariochromene B and C1)

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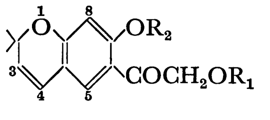
Condensation of 7-hydroxy-2,2-dimethylchroman with benzoyloxyacetonitrile gave 7-hydroxy-6-benzoyloxyacetyl-2,2-dimethylchroman (**3**) which was converted into 7-hydroxy-6-acetoxyacetyl-2,2-dimethylchroman (**7**) in four steps. Dehydrogenation of **7** with DDQ in dried toluene afforded ripariochromene B (**1**). Ripariochromene B was also synthesized by oxidative cyclization of 2,4-dihydroxy-5-(3-methyl-2-butenyl)-ω-acetoxyacetophenone (**13**) which was prepared from resorcinol and acetoxyacetonitrile in two steps. Ripariochromene C (**2**) was synthesized from resorcinol by the same method as that described above.

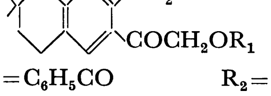
Ripariochromene B and ripariochromene C have recently been isolated from Australian *Eupatorium riparium* Regel along with several other chromenes, and these structures have been determined to be respectively 7-hydroxy-6-acetoxyacetyl-2,2-dimethylchromene (**1**) and 7-hydroxy-6-isobutyryloxyacetyl-2,2-dimethylchromene (**2**) which have an acyloxyacetyl substituent at the 6-position on the basis of spectral evidence.2) In the present paper, the syntheses of **1** and **2** are reported to confirm the proposed structures of natural ripariochromene B and C.



(**1**) $R_1=CH_3CO$ $R_2=H$
(**2**) $R_1=(CH_3)_2CHCO$ $R_2=H$
(**8**) $R_1=R_2=CH_3CO$
(**11**) $R_1=(CH_3)_2CHCO$ $R_2=CH_3CO$

Fig. 1.

The condensation of 7-hydroxy-2,2-dimethylchroman3) with benzoyloxyacetonitrile in the presence of freshly-fused zinc chloride gave 7-hydroxy-6-benzoyloxyacetyl-2,2-dimethylchroman (**3**), which produced a dark-brown reaction in the ferric chloride color test. Chroman **3** was easily converted into a 7-(benzyloxy) chroman derivative (**4**) upon treatment with benzyl chloride. Compound **4** was hydrolyzed with diluted hydrochloric acid in ethanol to give a 6-(hydroxyacetyl) chroman derivative (**5**) which showed absorption bands attributable to an alcoholic hydroxyl group in the IR spectrum and no proton signals from the benzoyl group in the NMR spectrum. The hydrolysis of **4** with a diluted alkali, however, did not afford the desired chroman derivative **5**. Compound **5**, after being converted into a 6-(acetoxyacetyl)chroman derivative (**6**) with acetyl chloride in a large quantity of pyridine cooled by ice, was subjected to hydrogenolysis over palladium on charcoal in methanol to afford a 7-(hydroxy)chroman derivative (dihydroripariochromene B) (**7**), which produced a light-brown reaction in the ferric chloride color test and indicated an intramolecular hydrogen-bonded hydroxyl group in the NMR spectrum. The dehydrogenation4—6) of **7** with boiling in DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone) in dried toluene afforded the desired chromene (**1**) (mp 146—147 °C) (lit, mp 145—146 °C).2) This compound was further converted into the acetate of ripariochromene B (**8**).



(**3**) $R_1=C_6H_5CO$ $R_2=H$
(**4**) $R_1=C_6H_5CO$ $R_2=C_6H_5CH_2$
(**5**) $R_1=H$ $R_2=C_6H_5CH_2$
(**6**) $R_1=CH_3CO$ $R_2=C_6H_5CH_2$
(**7**) $R_1=CH_3CO$ $R_2=H$
(**9**) $R_1=(CH_3)_2CHCO$ $R_2=C_6H_5CH_2$
(**10**) $R_1=(CH_3)_2CHCO$ $R_2=H$

Fig. 2.

According to the procedure described above, **5** was treated with isobutyryl chloride to give a 6-(isobutyryloxyacetyl)chroman derivative (**9**). The subsequent hydrogenolysis of **9** afforded a 7-(hydroxy)chroman derivative (dihydroripariochromene C) (**10**). The dehydrogenation of **10** with DDQ gave the desired chromene (**2**) (mp 109.5—110.5 °C) (lit, mp 109—110 °C).2) Chromene **2** was also converted into the acetate of ripariochromene C (**11**).

Chromenes **1** and **2** thus synthesized were respectively confirmed to be identical to natural ripariochromene B and C on the basis of a mixed melting-point determination and NMR, IR, and UV spectral comparisons.

In order to provide an alternate approach to the synthesis of chromenes **1** and **2**, another route was investigated. The condensation of resorcinol with acetoxyacetonitrile or isobutyryloxyacetonitrile in the presence of freshly-fused zinc chloride easily gave ω-(acyloxy)acetophenones (**12**) or (**16**), respectively, which showed a positive reaction in the ferric chloride color test and was supported by IR and NMR spectra. The BF_3-catalyzed condensation of 2-methyl-3-buten-2-ol7) with **12** or **16** afforded 3- or 5-(3-methyl-2-butenyl)-ω-(acyloxy)acetophenones (**13** and **14**) or (**17** and **18**), respectively, which were isolated by column chromatography. All these compounds showed positive reactions in the ferric chloride color test, and these structures were supported by NMR spectra. The major product **13** or **17**, in each condensation, was boiled with DDQ in dried toluene for conversion into chromene **1** or **2**, which was confirmed to be identical with the ripariochromene B or C synthesized above, respectively. The minor products **14** and **18** in the condensation were similary treated to give compounds **15** and **19**, whose structures were revealed by their NMR spectra to be chromenes.

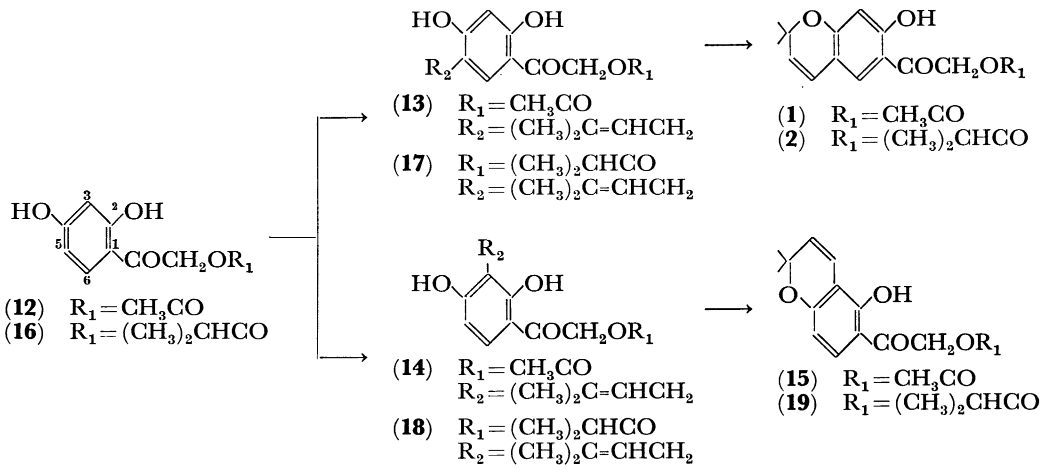


Fig. 3.

Experimental

All the melting points are uncorrected. The IR spectra were taken on a Hitachi 215 Spectrophotometer and the UV spectra on a Hitachi 124 Spectrophotometer. The NMR spectra were measured with a JOEL PS-100 Spectrometer (100 MHz), using tetramethylsilane as an internal standard (δ, ppm). Column chromatography was carried out on Kieselgel 60 (70—230 mesh) (Merck).

7-Hydroxy-6-benzoyloxyacetyl-2,2-dimethylchroman (3). 7-Hydroxy-2,2-dimethylchroman (10.6 g), anhydrous benzoyloxyacetonitrile (14.5 g), and freshly-fused zinc chloride (4 g) were successively added in dried ether (60 ml), and a rapid stream of dried hydrogen chloride was bubbled into the mixture with stirring and cooling in an ice-salt bath for 7 h. The reaction mixture was allowed to stand for 24 h in a refrigerator, and then the solvent was decanted. The residual solid, after being washed with dried ether (80 ml), was boiled in water (80 ml) for 1 h and cooled to give a white precipitate, which was collected and recrystallized from methanol as colorless needles (**3**) (15.2 g, 75%): mp 141—142 °C; IR ν_{max}^{KBr} 1720, 1665 cm^{-1}; NMR (CDCl$_3$) δ 1.36 (s, 6H, 2×CH$_3$), 1.83 (t, 2H, J=7 Hz, C$_3$-H), 2.73 (t, 2H, J=7 Hz, C$_4$-H), 5.48 (s, 2H, CH$_2$), 6.32 (s, 1H, arom. H), 7.3—7.6 (m, 4H, arom. H), 8.0—8.3 (m, 2H, arom. H), 11.66 (s, OH). Found: C, 70.55; H, 5.85%. Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92%.

7-Benzyloxy-6-benzoyloxyacetyl-2,2-dimethylchroman (4). Compound **3** (10.2 g), benzyl chloride (7.0 g), potassium iodide (9.0 g), and dried potassium carbonate (15.0 g) were successively added to dried acetone (150 ml). After the mixture was heated under reflux for 7 h, the solvent was evaporated under reduced pressure, and the residual substance was poured into cold water. The white precipitate thus formed was collected and recrystallized from ethanol to give colorless needles (**4**) (11.6 g, 90%): mp 146—147 °C; IR ν_{max}^{KBr} 1725, 1662 cm^{-1}; NMR (CDCl$_3$) δ 1.36 (s, 6H, 2×CH$_3$), 1.83 (t, 2H, J=7 Hz, C$_3$-H), 2.73 (t, 2H, J=7 Hz, C$_4$-H), 5.11 (s, 2H, $\underline{CH_2}C_6H_5$), 5.34 (s, 2H, CH$_2$), 6.45 (s, 1H, C$_8$-H), 7.3—7.6 (m, 8H. arom. H), 7.79 (s, 1H, C$_5$-H), 8.0—8.2 (m, 2H, arom. H). Found: C, 75.36; H, 6.04%. Calcd for $C_{27}H_{26}O_5$: C, 75.33; H, 6.09%.

7-Benzyloxy-6-hydroxyacetyl-2,2-dimethylchroman (5). Compound **4** (8.6 g) with *ca.* 18% hydrochloric acid (80 ml) in ethanol (400 ml) was refluxed for 8 h, and then the organic solvent was removed under reduced pressure. The precipitate was recrystallized from methanol to give colorless needles (**5**) (2.7 g, 40%): mp 142—143 °C; IR ν_{max}^{KBr} 3480, 1643 cm^{-1}; NMR (CDCl$_3$) δ 1.37 (s, 6H, 2×CH$_3$), 1.83 (t, 2H, J=7 Hz, C$_3$-H), 2.75 (t, 2H, J=7 Hz, C$_4$-H), 4.63 (s, 2H, CH$_2$), 5.05 (s, 2H, $\underline{CH_2}C_6H_5$), 6.43 (s, 1H, C$_8$-H), 7.36 (s, 5H, arom. H), 7.87 (s, 1H, C$_5$-H). Found: C, 73.63; H, 6.74%. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79%.

7-Benzyloxy-6-acetoxyacetyl-2,2-dimethylchroman (6). To a solution of **5** (1.0 g) in dried pyridine (25 ml) was added acetyl chloride (1.5 ml) drop by drop with stirring and cooling in an ice bath, and the mixture was stirred with cooling for 6 h. The reacted mixture was poured into ice-cold water (20 ml) to give a white precipitate, which was collected and recrystallized from methanol as colorless needles (**6**) (0.76 g, 65%): mp 111—112 °C; IR ν_{max}^{KBr} 1740, 1662 cm^{-1}; NMR (CDCl$_3$) δ 1.32 (s, 6H, 2×CH$_3$), 1.78 (t, 2H, J=7 Hz, C$_3$-H), 2.72 (t, 2H, J=7 Hz, C$_4$-H), 2.14 (s, 3H, CH$_3$CO), 5.06 and 5.10 (each s, 2H, $\underline{CH_2}C_6H_5$ and COCH$_2$O), 6.41 (s, 1H, C$_8$-H), 7.41 (s, 5H, arom. H), 7.76 (s, 1H, C$_5$-H). Found: C, 71.90; H, 6.68%. Calcd for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57%.

7-Hydroxy-6-acetoxyacetyl-2,2-dimethylchroman (Dihydroripariochromene B) (7). Compound **6** (0.74 g) was hydrogenated over palladium on charcoal (10%; 0.18 g) in methanol until the uptake of hydrogen ceased. The solvent was removed under reduced pressure, and the residue was recrystallized from methanol to give colorless plates (**7**) (0.37 g, 70%): mp 131—132 °C; IR ν_{max}^{KBr} 1745, 1645 cm^{-1}; NMR (CDCl$_3$) δ 1.34 (s, 6H, 2×CH$_3$), 1.81 (t, 2H, J=7 Hz, C$_3$-H), 2.71 (t, 2H, J=7 Hz, C$_4$-H), 2.21 (s, 3H, CH$_3$CO), 5.24 (s, 2H, CH$_2$), 6.31 (s, 1H, C$_8$-H), 7.30 (s, 1H, C$_5$-H), 11.80 (s, OH). Found: C, 64.87; H, 6.59%. Calcd for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52%.

7-Hydroxy-6-acetoxyacetyl-2,2-dimethylchromene (Ripariochromene B) (1). A mixture of **7** (0.11 g) and DDQ (0.10 g) in dried toluene (50 ml) was heated under reflux for 10 h, and then the solvent was removed under reduced pressure. The residual substance was purified by column chromatography over silica gel with chloroform to give chromene **1**, which was recrystallized from carbon tetrachloride as colorless needles (40 mg, 40%): mp 146—147 °C (no depression in a mixed melting-point determination with natural ripariochromene B); IR ν_{max}^{KBr} 1750, 1652 cm^{-1}; UV λ_{max}^{EtOH} nm (log ε) 257 (4.51), 286 (3.95), 347 (3.85). NMR (CDCl$_3$) δ 1.41 (s, 6H, 2×CH$_3$), 2.20 (s, 3H, CH$_3$CO), 5.20 (s, 2H, CH$_2$), 5.54 (d, 1H, J=9 Hz, C$_3$-H), 6.23 (d, 1H, J=9 Hz, C$_4$-H), 6.30 (s, 1H, C$_8$-H), 7.15 (s, 1H, C$_5$-H), 12.20 (s, OH). Found: C, 65.09; H, 5.79%. Calcd for

$C_{15}H_{16}O_5$: C, 65.21; H, 5.84%.

7-Acetoxy-6-acetoxyacetyl-2,2-dimethylchromene (Acetate of Ripariochromene B) (8). After a mixture of **1** (54 mg), acetic anhydride (1 ml), and pyridine had been allowed to stand over 24 h at room temperature, cold water was added to the mixture and it was again allowed to stand overnight in a refrigerator. The mixture was extracted with ether and the ethereal solution was washed with a saturated aqueous solution of sodium chloride, dried over sodium sulfate, and the solvent was evaporated. The residue was recrystallized from a mixture of benzene and hexane to give colorless needles (**8**) (58 mg, 93%): mp 109—110 °C; IR $\nu_{\max}^{\mathrm{KBr}}$ 1770, 1735, 1675 cm^{-1}; NMR ($CDCl_3$) δ 1.46 (s, 6H, 2×CH_3), 2.19 (s, 3H, CH_3CO), 2.35 (s, 3H, C_7–CH_3CO), 5.10 (s, 2H, CH_2), 5.64 (d, 1H, $J=10$ Hz, C_3–H), 6.29 (d, 1H, $J=10$ Hz, C_4–H), 6.53 (s, 1H, C_8–H), 7.46 (s, 1H, C_5–H). Found: C, 64.25; H, 5.68%. Calcd for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70%.

7-Benzyloxy-6-isobutyryloxyacetyl-2,2-dimethylchroman (9). Isobutyryl chloride (1.5 ml) was added to a solution of **5** (0.86 g) in dried pyridine (25 ml). After stirring in an ice bath for 10 h, the mixture was worked up in the same manner, as in the case of **6**, to give chroman **9**, which was recrystallized from methanol as colorless needles (0.76 g, 73%): mp 93—94 °C; IR $\nu_{\max}^{\mathrm{KBr}}$ 1740, 1680 cm^{-1}; NMR ($CDCl_3$) δ 1.23 [d, 6H, $J=7$ Hz, $(C\underline{H}_3)_2CH$], 1.32 (s, 6H, 2×CH_3), 1.77 (t, 2H, $J=7$ Hz, C_3–H), 2.71 (t, 2H, $J=7$ Hz, C_4–H), 2.65 [m, 1H, $(CH_3)_2C\underline{H}$], 5.06 and 5.09 (each s, 2H, $C\underline{H}_2C_6H_5$ and $COCH_2O$), 6.40 (s, 1H, C_8–H), 7.40 (s, 5H, arom. H), 6.77 (s, 1H, C_5–H). Found: C, 72.86; H, 6.84%. Calcd for $C_{24}H_{28}O_5$: C, 72.70; H, 7.12%.

7-Hydroxy-6-isobutyryloxyacetyl-2,2-dimethylchroman (Dihydroripariochromene C) (10). Compound **9** (0.44 g) was hydrogenated over palladium on charcoal and the reacted mixture was worked up in the same manner, as in the case of **7**, to give colorless plates (**10**) (0.26 g, 70%): mp 113—114 °C; IR $\nu_{\max}^{\mathrm{KBr}}$ 1738, 1640 cm^{-1}; NMR ($CDCl_3$) δ 1.24 [d, 6H, $J=7$ Hz, $(C\underline{H}_3)_2CH$], 1.33 (s, 6H, 2×CH_3), 1.80 (t, 2H, $J=7$ Hz, C_3–H), 2.70 (t, 2H, $J=7$ Hz, C_4–H), *ca.* 2.67 [m, 1H, $(CH_3)_2C\underline{H}$], 5.22 (s, 2H, CH_2), 6.30 (s, 1H, C_8–H), 7.30 (s, 1H, C_5–H), 11.80 (s, OH). Found: C, 66.62; H, 7.50%. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24%.

7-Hydroxy-6-isobutyryloxyacetyl-2,2-dimethylchromene (Ripariochromene C) (2). A mixture of **10** (102 mg), DDQ (85 mg), and dried toluene (30 ml) was heated under reflux for 9 h. The reacted mixture was worked up in the same manner, as in the case of **1**, to give chromene **2**, which was recrystallized from carbon tetrachloride as colorless needles (30 mg, 30%): mp 109.5—110.5 °C (no depression in a mixed melting-point determination with natural ripariochromene C); IR $\nu_{\max}^{\mathrm{KBr}}$ 1740, 1645 cm^{-1}; UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε) 257 (4.39), 287 (3.77), 348 (3.72); NMR ($CDCl_3$) δ 1.26 [d, 6H, $J=7$ Hz, $(C\underline{H}_3)_2CH$], 1.45 (s, 6H, 2×CH_3), 2.73 [m, 1H, $(CH_3)_2C\underline{H}$], 5.24 (s, 2H, CH_2), 5.57 (d, 1H, $J=9$ Hz, C_3–H), 6.25 (d, 1H, $J=9$ Hz, C_4–H), 6.33 (s, 1H, C_8–H), 7.18 (s, 1H, C_5–H), 12.05 (s, OH). Found: C, 67.37; H, 6.58%. Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62%.

7-Acetoxy-6-isobutyryloxyacetyl-2,2-dimethylchromene (Acetate of Ripariochromene C) (11). A mixture of **2** (54 mg), acetic anhydride (1 ml), and pyridine was worked up in the same manner, as in the case of **8**, to give colorless needles (**11**) (56 mg, 91%): mp 124—125 °C; IR $\nu_{\max}^{\mathrm{KBr}}$ 1775, 1740, 1685 cm^{-1}; NMR ($CDCl_3$) δ 1.24 [d, 6H, $J=7$ Hz, $(C\underline{H}_3)_2CH$], 1.46 (s, 6H, 2×CH_3), 2.35 (s, 3H, CH_3CO), 2.70 [m, 1H, $(CH_3)_2C\underline{H}$], 5.07 (s, 2H, CH_2), 5.63 (d, 1H, $J=10$ Hz, C_3–H), 6.29 (d, 1H, $J=10$ Hz, C_4–H), 6.52 (s, 1H, C_8–H), 7.48 (s, 1H, C_5–H). Found: C, 65.88; H, 6.32%. Calcd for $C_{19}H_{22}O_6$: C, 65.88; H, 6.40%.

2,4-Dihydroxy-ω-(acetoxy)acetophenone (12). Resorcionl (20 g), acetoxyacetonitrile (26.5 g), and zinc chloride (8 g) were successively added to dried ether (100 ml), and a rapid stream of dried hydrogen chloride was bubbled into the mixture with stirring in an ice-salt bath for 2 h. The mixture, after being treated in the same manner as in the case of **3**, was heated in water–methanol (1 : 9; 300 ml) for 1.5 h at 60 °C, and the solvent was distilled out under reduced pressure. The residue was recrystallized from chloroform to give colorless plates (**12**) (15 g, 40%), producing a light-brown reaction in the ferric chloride color test: mp 167—168 °C; IR $\nu_{\max}^{\mathrm{KBr}}$ 1740, 1610 cm^{-1}; NMR (DMSO) δ 2.13 (s, 3H, CH_3CO), 5.24 (s, 2H, CH_2), 6.30 (bs, 1H, C_3–H), 6.35 [q, 1H, ($J=2.5$, 9 Hz) C_5–H], 7.68 (d, 1H, $J=9$ Hz, C_6–H), 10.63 (s, C_4–OH), 11.54 (s, C_2–OH). Found: C, 57.03; H, 4.77%. Calcd for $C_{10}H_{10}O_5$: C, 57.14; H, 4.80%.

5-(3-Methyl-2-butenyl)-2,4-dihydroxy-ω-(acetoxy)acetophenone (13) and 3-(3-Methyl-2-butenyl)-2,4-dihydroxy-ω-(acetoxy)acetophenone (14). To a mixed solution of **12** (5.0 g) and boron trifluoride etherate (3.3 g) in dried dioxane (70 ml) was gradually added a solution of 2-methyl-3-buten-2-ol (2.1 g) in dried dioxane (15 ml) and the mixture was heated at 50—60 °C for 3 h. The reacted mixture was cooled to room temperature, poured into cold water, and taken up in ether. The ethereal solution was washed with an aqueous solution of sodium hydrogen carbonate, dried over sodium sulfate, and the solvent was evaporated to give a yellow oil, which was chromatographed over a silica-gel column with chloroform with separation of compounds A ($R_f=0.19$) and B ($R_f=0.07$). Compound B was recrystallized from benzene as colorless needles (**13**) (1.8 g, 20%): mp 129—130 °C; IR $\nu_{\max}^{\mathrm{KBr}}$ 1740, 1630 cm^{-1}; NMR ($CDCl_3$) δ 1.77 (bs, 6H, 2×CH_3), 2.23 (s, 3H, CH_3CO), 3.24 (d, 2H, $J=7$ Hz, $C\underline{H}_2CH{=}$), 5.24[8] (s, 2H, CH_2), *ca.* 5.24[8] [1H, $(CH_3)_2C{=}C\underline{H}$], 6.31 (s, 2H, C_3–H, C_4–OH), 7.25 (s, 1H, C_6–H), 11.93 (s, C_2–OH). Found: C, 64.77; H, 6.43%. Calcd for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52%.

Compound A was recrystallized from benzene as colorless needles (**14**) (0.4 g, 6%), producing a positive reaction in the ferric chloride color test: mp 147—148 °C; IR $\nu_{\max}^{\mathrm{KBr}}$ 1725, 1630 cm^{-1}; NMR ($CDCl_3$) δ 1.74 (s, 3H) and 1.80 (s, 3H) [$(C\underline{H}_3)_2C{=}CH$], 2.22 (s, 3H, CH_3CO), 3.39 (d, 2H, $J=7$ Hz, $C\underline{H}_2CH{=}$), 5.22[8] (s, 2H, CH_2), *ca.* 5.22[8] [1H, $(CH_3)_2C{=}C\underline{H}$], 6.32 (d, 1H, $J=9$ Hz, C_5–H), 6.37 (s, C_4–OH), 7.83 (d, 1H, $J=9$ Hz, C_6–H), 12.45 (s, C_2–OH). Found: C, 64.68; H, 6.41%. Calcd for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52%.

Another Synthesis of Ripariochromene B (1). A mixture of **13** (0.30 g), DDQ (0.32 g), and dried toluene (120 ml) was heated under reflux for 2 h. The reacted mixture was worked up in the same manner as in the case of chromene **1**. The chromene thus obtained was recrystallized from carbon tetrachloride as colorless needles (**1**) (0.18 g, 65%): mp 146—147 °C (no depression in a mixed melting-point determination with the ripariochromene B synthesized above).

5-Hydroxy-6-acetoxyacetyl-2,2-dimethylchromene (15). A mixture of **14** (57 mg), DDQ (68 mg), and dried toluene (20 ml) was worked up in the same manner described above. The chromene thus obtained was crystallized from petroleum ether (35—40 °C) as colorless prisms (**15**) (24 mg, 42%): mp 117—118.5 °C; IR $\nu_{\max}^{\mathrm{KBr}}$ 1755, 1660 cm^{-1}; NMR ($CDCl_3$) δ 1.44 (s, 6H, 2×CH_3), 2.21 (s, 3H, CH_3CO), 5.23 (s, 2H, CH_2), 5.56 (d, 1H, $J=10$ Hz, C_3–H), 6.32 (d, 1H, $J=10$ Hz, C_4–H), 6.67 (d, 1H, $J=10$ Hz, C_8–H), 7.38 (d, 1H, $J=10$ Hz, C_7–H), 12.32 (s, OH). Found: C, 65.10; H, 5.90%. Calcd for $C_{15}H_{16}O_5$: C, 65.21; H, 5.84%.

*2,4-Dihydroxy-ω-(isobutyryloxy)acetophenone (**16**).* A mixture of resorcinol (10.4 g), isobutyryloxyacetonitrile (18 g), and zinc chloride (6 g) in dried ether (200 ml) was worked up in the same manner as in the case of **12** to give colorless prisms (**16**) (10 g, 40%): mp 116—117 °C; IR ν_{max}^{KBr} 1710, 1635 cm^{-1}; NMR (DMSO) δ 1.15 [d, 6H, J=7 Hz, $(C\underline{H}_3)_2CH$], 2.63 [m, 1H, $(CH_3)_2C\underline{H}$], 5.23 (s, 2H, CH_2), 6.28 (bs, 1H, C_3–H), 6.33 [q, 1H, (J=2.5, 9 Hz) C_5–H], 7.68 [d, 1H, (J=9 Hz) C_6–H], 10.57 (s, C_4–OH), 11.46 (s, C_2–OH). Found: C, 60.46; H, 5.74%. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92%.

*5-(3-Methyl-2-butenyl)-2,4-dihydroxy-ω-(isobutyryloxy)acetophenone (**17**) and 3-(3-Methyl-2-butenyl)-2,4-dihydroxy-ω-(isobutyryloxy)acetophenone (**18**).* A mixed solution of **16** (8.0 g), boron trifluoride etherate (3.6 g), and 2-methyl-3-buten-2-ol (2.1 g) in dried dioxane (150 ml) was worked up in the same manner as in the case of **13** to give **17** and **18**. Compound **17** was recrystallized from benzene as colorless needles (1.8 g. 20%): mp 122—123 °C; IR ν_{max}^{KBr} 1720, 1650 cm^{-1}; NMR ($CDCl_3$) δ 1.27 [d, 6H, J=7 Hz, $(C\underline{H}_3)_2CH$], 1.74 [bs, 6H, $(C\underline{H}_3)_2C=CH$], 2.74 [m, 1H, $(CH_3)_2C\underline{H}$], 3.23 [d, 2H, J=7 Hz, $C\underline{H}_2CH=$], 5.23[8] (s, 2H, CH_2), *ca.* 5.23[8] [1H, $(CH_3)_2C=C\underline{H}$], 6.29 (s, 1H, C_3–H), 6.47 (s, C_4–OH), 7.25 (s, 1H, C_6–H), 11.96 (s, C_2–OH). Found: C, 66.88; H, 7.29%. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24%.

Recrystallization of **18** from benzene gave colorless needles (0.4 g, 5%): mp 147—148 °C; IR ν_{max}^{KBr} 1713, 1625 cm^{-1}; NMR ($CDCl_3$) δ 1.25 [d, 6H, J=7 Hz, $(C\underline{H}_3)_2CH$], 1.73 (s, 3H) and 1.79 (s, 3H) [$(C\underline{H}_3)_2C=CH$], 2.73 [m, 1H, $(CH_3)_2C\underline{H}$], 3.40 (d, 2H, J=7 Hz, $C\underline{H}_2CH=$), 5.24[8] (s, 2H, CH_2), *ca.* 5.24[8] [1H, $(CH_3)_2C=C\underline{H}$], 6.35 (d, 1H, J=9 Hz, C_5–H), 6.39 (s, C_4–OH), 7.36 (d, 1H, J=9 Hz, C_6–H), 12.45 (s, C_2–OH). Found: C, 66.50; H, 7.12%. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24%.

*Another Synthesis of Ripariochromene C (**2**).* A mixture of **17** (0.30 g), DDQ (0.29 g), and dried toluene (120 ml) was worked up in the manner described above to give colorless needles (**2**) (0.18 g, 60%): mp 109.5—110.5 °C (no depression in a mixed melting-point determination with the ripariochromene C synthesized above).

*5-Hydroxy-6-isobutyryloxyacetyl-2,2-dimethylchromene (**19**).* A mixture of **18** (102 mg), DDQ (113 mg), and dried toluene (120 ml) was worked up in the manner described above to give colorless prisms (**19**) (53 mg, 52%): mp 72—73.5 °C; IR ν_{max}^{KBr} 1735, 1640 cm^{-1}; NMR ($CDCl_3$) δ 1.26 [d, 6H, J=7 Hz, $(C\underline{H}_3)_2CH$], 1.44 (s, 6H, $2\times CH_3$), 2.73 [m, 1H, $(CH_3)_2C\underline{H}$], 5.22 (s, 2H, CH_2), 5.55 (d, 1H, J=10 Hz, C_3–H), 6.32 (d, 1H, J=10 Hz, C_4–H), 6.68 (d, 1H, J=10 Hz, C_8–H), 7.38 (d, 1H, J=10 Hz, C_7–H), 12.33 (s, OH). Found: C, 67.36; H, 6.72%. Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62%.

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