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# Synthesis of Carboxy-2,2-dimethylchromans and Chromenes

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The condensation of hydroxybenzoic acids, viz., 2,5-dihydroxy-, 3,5-dihydroxy-, 3,4,5-trihydroxy- and 2,4,6-trihydroxybenzoic acid with 2-methylbut-1,3-diene (isoprene) in presence of orthophosphoric acid giving corresponding carboxy-2,2-dimethylchromans is described. 2,2-Dimethylchromans have been dehydrogenated with *DDQ* to give corresponding carboxy-2,2-dimethylchromenes.

*(Keywords: Carboxy-2,2-dimethylchromans; Carboxy-2,2-dimethylchromenes; 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone; Gallic acid; Gentisic acid; 2-Methylbut-1,3-diene)*

*Synthese von Carboxy-2,2-dimethylchromanen und -chromenen*

Die Kondensation von 2,5-Dihydroxy-, 3,5-Dihydroxy-, 3,4,5-Trihydroxy- und 2,4,6-Trihydroxybenzoesäuren mit 2-Methyl-1,3-butadien (Isopren) in Gegenwart von Orthophosphorsäure ergab die jeweils korrespondierenden Carboxy-2,2-dimethylchromane. Dehydrogenierung mit *DDQ* führte zu den entsprechenden Carboxy-2,2-dimethylchromanen.

## Introduction

Carboxy-2,2-dimethylchromans and chromenes occur very infrequently among natural products; the only example known so far is β-tubaic acid (**1**), isolated by *Yoshihiko* et al.[1] from the roots of *Derris elliptica* and has been shown to exhibit antimicrobial activity. However, they are obtained as degradation product in the course of structure elucidation of a number of naturally occurring prenylated compounds[2–10]. Besides, they can be used as starting material for the synthesis of pyranobenzophenones and pyranoxanthones[11].



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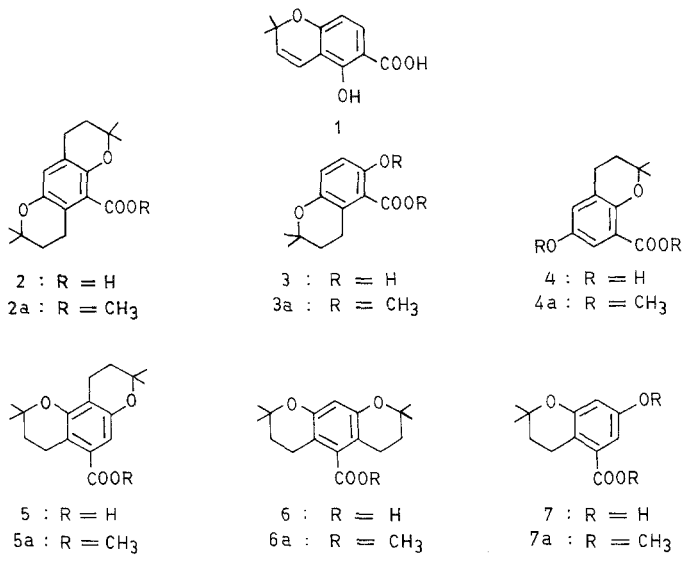
Earlier carboxy-2,2-dimethylchromans and chromenes have been prepared by (i) condensation of appropriate phenol with 2-hydroxy-2-methylbut-3-yne[12] (ii) oxidation of formyl substituted 2,2-dimethylchromans[13] (iii) *Clemmenson* reduction of 2,2-dimethylchroman-4-ones[14] and (iv) acid catalysed[10,11] and oxidative[2] cyclization of the appropriate C-prenyl derivatives. Method (i) is of historic importance only as the yields obtained are seldom more than 2-3%. Method (ii)-(iv) suffer from the disadvantage that the appropriate starting materials are difficult to prepare. Thus a convenient method for their synthesis was desired.

In this paper, we describe a convenient one step synthesis for carboxy-2,2-dimethylchromans involving condensation of hydroxybenzoic acids with 2-methylbut-1,3-diene[15–17] (isoprene) in presence of orthophosphoric acid. The reaction has been carried out with 2,5-dihydroxy-, 3,5-dihydroxy-, 3,4,5-trihydroxy- and 2,4,6-trihydroxybenzoic acid.

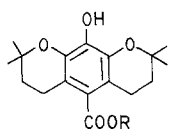
## Results and Discussion

Condensation of 2,5-dihydroxybenzoic acid (gentisic acid) with isoprene in presence of orthophosphoric acid gave a mixture of three products **A**, **B** and **C** in the ratio of 1:3:6 (overall yield 75%), which were separated by column chromatography over silica gel. The faster moving compound **A** gave negative ferric reaction and its elemental analysis showed the introduction of two isoprene units. The $^1$H-NMR spectrum of **A** showed two singlets at $\delta$ 1.28 and 1.39 ppm (each integrating for six protons, *gem*-dimethyl groups), a multiplet at 1.60-1.90 (two methylene groups), two distinct triplets at 2.74 and 3.06 ($J = 7$ Hz, each integrating for two protons, methylene groups) and a singlet of one proton at 6.58 (aromatic proton). It was thus assigned the structure 2,2,7,7-tetramethyl-3,4,8,9-tetrahydro-2*H*, 7*H*-benzo [1,2—*b*:4,5—*b'*]dipyran-10-carboxylic acid (**2**). The $^1$H-NMR spectrum of compound **B**—which gave a positive ferric reaction—showed the signals characteristic for a 2,2-dimethylchroman ring. The two aromatic protons appeared as doublets ($J = 9$ Hz) at 6.72 and 6.95 ppm. It was therefore assigned the structure as 6-hydroxy-2,2-dimethyl-3,4-dihydro-2*H*-1-benzopyran-5-carboxylic acid (**3**). The third compound **C** was found to be an isomer of **3** on elemental analysis but gave negative ferric reaction. It was assigned the structure 6-hydroxy-2,2-dimethyl-3,4-dihydro-2*H*-1-benzopyran-8-carboxylic acid (**4**) on the basis of its $^1$H-NMR spectrum which showed the presence of two *meta* coupled aromatic protons as doublets ($J = 2.5$ Hz) at 6.94 and 7.41.

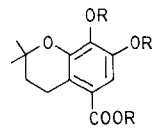



3,5-Dihydroxybenzoic acid gave by a similar condensation with isoprene three products **D**, **E** and **F** in the ratio of 1:1:3 (overall yield 60%), which were separated by column chromatography over silica gel. Compound **D** and **E** were found to be isomeric dichromans from their elemental analysis. The $^1$H-NMR spectrum of compound **D** showed, besides other signals, methylene protons as multiplet and two triplets at 1.65-1.95 (four protons), 2.70 and 3.05 (each integrating for two protons) respectively, whereas only two triplets, of four protons each, at 1.83 and 2.80 were observed in the $^1$H-NMR spectrum of compound **E**. Compound **D** was, therefore, assigned the angular dichroman structure, 2,2,8,8-tetramethyl-3,4,9,10-tetrahydro-2*H*,8*H*-benzo[1,2—*b*:3,4—*b*']dipyran-5-carboxylic acid (**5**) and **E** was assigned the symmetrical, linear dichroman structure, 2,2,8,8-tetramethyl-3,4,6,7-tetrahydro-2*H*,8*H*-benzo[1,2—*b*:5,4—*b*']dipyran-5-carboxylic acid (**6**). Elemental analysis of third compound **F** indicated introduction of only one isoprene unit and was assigned the structure 7-hydroxy-2,2-dimethyl-3,4-dihydro-2*H*-1-benzopyran-5-carboxylic acid (**7**) on the basis of its $^1$H-NMR spectrum which showed, besides other signals, two meta coupled aromatic protons as two doublets at 6.57 and 7.11 ($J = 2.5$ Hz).

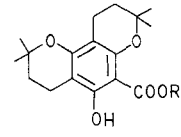
Similarly, condensation of 3,4,5-trihydroxybenzoic acid (gallic acid) with isoprene gave a mixture of two products, 10-hydroxy-2,2,8,8-



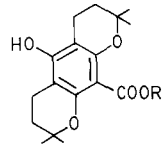

8 : R = H
8a : R = $CH_3$



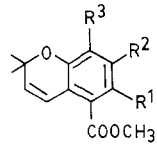

9 : R = H
9a : R = $CH_3$



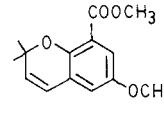

10 : R = H
10a : R = $CH_3$




11 : R = H
11a : R = $CH_3$




12 : $R^1 = OCH_3$, $R^2 = R^3 = H$
13 : $R^1 = R^3 = H$, $R^2 = OCH_3$
14 : $R^1 = H$, $R^2 = R^3 = OCH_3$

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tetramethyl-3,4,6,7-tetrahydro-2*H*,8*H*-benzo [1,2—*b*:5,4—*b*'] dipyran-5-carboxylic acid (**8**) and 7,8-dihydroxy-2,2-dimethyl-3,4-dihydro-2*H*-1-benzopyran-5-carboxylic acid (**9**) in the ratio of 1:4 (overall yield 70%), which were separated by column chromatography. These structures were assigned on the basis of elemental analysis and $^1$H-NMR spectral data.

2,4,6-Trihydroxybenzoic acid, when treated similarly, gave a mixture of two products, 5-hydroxy-2,2,8,8-tetramethyl-3,4,9,10-tetrahydro-2*H*,8*H*-benzo[1,2—*b*:3,4—*b*']dipyran-6-carboxylic acid (**10**) and 5-hydroxy-2,2,8,8-tetramethyl-3,4,6,7-tetrahydro-2*H*,8*H*-benzo [1,2—*b*:5,4—*b*']dipyran-10-carboxylic acid (**11**) in the ratio of 3:2 (overall yield 50%), which were separated by column chromatography. The assigned structures were in agreement with their elemental analysis and $^1$H-NMR spectral data. Unsymmetrical dichroman (**10**) gave a positive ferric reaction and exhibited in the $^1$H-NMR spectrum of its methyl ester (**10a**) a sharp low field singlet at 12.16 (1H, exchanged with $D_2O$) assignable to a chelated hydroxyl group. However the symmetrical dichroman **11** gave a negative ferric reaction and the hydroxyl group appeared at 5.49 in the $^1$H-NMR spectrum of its methyl ester **11a**.

Compound **3** on methylation gave methyl 6-methoxy-2,2-dimethyl-3,4-dihydro-2*H*-1-benzopyran-5-carboxylate (**3a**), which on reaction with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (*DDQ*) in refluxing benzene gave a product (80%), which was assigned the structure methyl

6-methoxy-2,2-dimethyl-2*H*-1-benzopyran-5-carboxylate (**12**) on the basis of its $^1$H-NMR spectral data, which showed a characteristic pair of doublets ($J = 10$ Hz) at 5.60 and 6.21 besides other signals. Similar dehydrogenation of **4a** (methyl ether of **4**), **7a** (methyl ether of **7**) and **9a** (methyl ether of **9**) with *DDQ* gave corresponding carboxy-2,2-dimethylchromenes; **15**, **13**, and **14** respectively.

## Acknowledgement

Our thanks are due to UGC, New Delhi, India, for financial assistance.

## Experimental

All melting points are uncorrected. $^1$H-NMR spectra were recorded on a Perkin-Elmer R-32 (90 MHz) spectrometer for solutions in $CDCl_3$ with $SiMe_4$ as internal standard. Silica gel (60–120 mesh) was used for all chromatographic separations.

### *Reaction of 2,5-Dihydroxybenzoic Acid with Isoprene*

#### *General Procedure*

A solution of isoprene (1.0 ml, 10.0 mmol) in xylene (4.0 ml) was added to a mixture of 2,5-dihydroxybenzoic acid (1.0 g, 6.5 mmol) orthophosphoric acid (85%, 2.0 ml) and xylene (2.0 ml) with constant stirring at 30–35 °C during 2 h. Stirring was continued for further 6 h and then ether (100.0 ml) added. The ether layer was washed with water, dried ($Na_2SO_4$) and distilled. The residue was chromatographed on silica gel while elution was effected with benzene—petroleum ether (7:3), benzene and benzene—ethyl acetate (19:1) successively to give

(i) 2,2,7,7-Tetramethyl-3,4,8,9-tetrahydro-2*H*,7*H*-benzo[1,2—*b*:4,5—*b*']dipyran-10-carboxylic acid (**2**); yield: 0.1 g (7.5%), m.p. 164–165 °C (Lit.[18] m.p. 161–163 °C).

(ii) 6-Hydroxy-2,2-dimethyl-3,4-dihydro-2*H*-1-benzopyran-5-carboxylic acid (**3**); yield: 0.3 g (22.5%), m.p. 195–196 °C (Lit.[18] m.p. 179–182 °C).

(iii) 6-Hydroxy-2,2-dimethyl-3,4-dihydro-2*H*-1-benzopyran-8-carboxylic acid (**4**); yield: 0.6 g (45.0%), m.p. 183–184 °C.

### *Methyl 6-Methoxy-2,2-dimethyl-3,4-dihydro-2H-1-benzopyran-5-carboxylate* (**3a**)

#### *General Procedure for Methylation*

**3** (0.2 g, 0.8 mmol) in dry acetone (40.0 ml) was refluxed with $Me_2SO_4$ (0.16 ml, 1.65 mmol) in presence of anhyd. $K_2CO_3$ (0.8 g) for 8 h. Inorganic salts were filtered and washed with more acetone. The combined filtrate distilled and the residue treated with crushed ice. The separated solid was then crystallised from petroleum ether to give **3a** as colourless plates (0.18 g), m.p. 71–72 °C. For other products see Table 1.

Table 1. *Synthesis and properties*

| Compound | Yield[a] [%] | M.p. [°C] | Molecular formula[k] |
|---|---|---|---|
| **2b** | 7.5[h] | 164-165 (161-163)[18] | $C_{17}H_{22}O_4$ |
| **3b** | 22.5[h] | 195-196 (179-182)[18] | $C_{12}H_{14}O_4$ |
| **4b** | 45.0[h] | 183-184 | $C_{12}H_{14}O_4$ |
| **5c** | 12.0[h] | 204-205 (204-205)[10] | $C_{17}H_{22}O_4$ |
| **6c** | 12.0[h] | 240-241 (209-210)[10] | $C_{17}H_{22}O_4$ |
| **7c** | 36.0[h] | 170-171 (171-172)[18] | $C_{12}H_{14}O_4$ |
| **8d** | 14[h] | 229-230 | $C_{17}H_{22}O_5$ |
| **9d** | 5.6[h] | 217-218 | $C_{12}H_{14}O_5$ |
| **10e** | 30[h] | 163-164 | $C_{17}H_{22}O_5$ |
| **11e** | 20[h] | 200-201 | $C_{17}H_{22}O_5$ |
| **2a** | 90[g] | 110-111 | $C_{18}H_{24}O_4$ |
| **3a** | 85[g] | 71–72 | $C_{14}H_{18}O_4$ |
| **4a** | 82 | oil | $C_{14}H_{18}O_4$ |
| **5a** | 95[g] | 82-83 (80-81)[10] | $C_{18}H_{24}O_4$ |
| **6a** | 86[g] | 140-141 (136-138)[10] | $C_{18}H_{24}O_4$ |
| **7a** | 90 | oil | $C_{14}H_{18}O_4$ |
| **8a** | 83[g] | 151-152 | $C_{18}H_{24}O_5$ |

*of the compounds prepared*

| $^1$H-NMR chemical shift, (δ/ppm, $J$ in Hz) |
|---|
| 1.28 and 1.39 (each s, each 6 H, 2 × C$Me_2$), 1.60–1.90 (m, 4 H, 3- and 8-H), 2.74 and 3.06 (each t, $J$ = 7 Hz, each 2 H, 4- and 9-H), and 6.58 (s, 1 H, 5-H). |
| 1.42 (s, 6 H, C$Me_2$), 1.89 and 3.15 (each t, $J$ = 7 Hz, each 2 H, 3- and 4-H), 6.72 and 6.95 (each d, $J$ = 9 Hz, each 1 H, 7- and 8-H)[i]. |
| 1.43 (s, 6 H, C$Me_2$), 1.88 and 2.76 (each t, $J$ = 7 Hz, each 2 H, 3- and 4-H), 6.94 and 7.41 (each d, $J$ = 2.5 Hz, each 1 H, 5- and 7-H)[i]. |
| 1.34 and 1.38 (each s, each 6 H, 2 × C$Me_2$), 1.65–1.95 (m, 4 H, 3- and 9-H), 2.70 and 3.05 (each t, $J$ = 7 Hz, each 2 H, 10- and 4-H), and 7.10 (s, 1 H, 6-H). |
| 1.37 (s, 12 H, 2 × C$Me_2$), 1.83 (t, $J$ = 7 Hz, 4 H, 3- and 7-H), 2.80 (t, $J$ = 7 Hz, 4 H, 4- and 6-H), and 6.30 (s, 1 H, 10-H)[i]. |
| 1.36 (s, 6 H, C$Me_2$), 1.82 and 3.02 (each t, $J$ = 7 Hz, each 2 H, 3- and 4-H), 6.57 and 7.11 (each d, $J$ = 2.5 Hz, each 1 H, 8- and 6-H)[i]. |
| 1.37 (s, 12 H, 2 × C$Me_2$), 1.82 (t, $J$ = 7 Hz, 4 H, 3- and 7-H), and 2.87 (t, $J$ = 7 Hz, 4 H, 4- and 6-H)[i]. |
| 1.27 (s, 6 H, C$Me_2$), 1.70 and 2.95 (each t, $J$ = 7 Hz, each 2 H, 3- and 4-H), and 7.24 (s, 1 H, 6-H)[i]. |
| 1.32 and 1.42 (each s, each 6 H, 2 × C$Me_2$), 1.69–1.94 (m, 4 H, 3- and 9-H), and 2.46–2.69 (m, 4 H, 4- and 10-H)[i]. |
| 1.33 (s, 12 H, 2 × C$Me_2$), 1.79 (t, $J$ = 7 Hz, 4 H, 3- and 7-H), and 2.44 (t, $J$ = 7 Hz, 4 H, 4- and 6-H)[i]. |
| 1.23 (s, 12 H, 2 × C$Me_2$), 1.60–1.79 (m, 4 H, 3- and 8-H),, 2.51–2.70 (m, 4 H, 4- and 9-H), 3.76 (s, 3 H, 10-$COOCH_3$), and 6.48 (s, 1 H, 5-H). |
| 1.34 (s, 6 H, C$Me_2$), 1.80 and 2.75 (each t, $J$ = 7 Hz, each 2 H, 3- and 4-H), 3.80 and 3.92 (each s, each 3 H, 6-$OCH_3$ and 5-$COOCH_3$), and 6.70 (s, 2 H, 7- and 8-H). |
| 1.31 (s, 6 H, C$Me_2$), 1.78 and 2.73 (each t, $J$ = 7 Hz, each 2 H, 3- and 4-H), 3.70 and 3.80 (each s, each 3 H, 6-$OCH_3$ and 8-$COOCH_3$), 6.67 and 7.05 (each d, $J$ = 2.5 Hz, each 1 H, 5- and 7-H). |
| 1.29 (s, 12 H, 2 × C$Me_2$), 1.72 (t, $J$ = 7 Hz, 4 H, 3- and 9-H), 2.60 and 3.00 (each t, $J$ = 7 Hz, each 2 H, 10- and 4-H), 3.78 (s, 3 H, 5-$COOCH_3$), and 6.96 (s, 1 H, 6-H). |
| 1.35 (s, 12 H, 2 × C$Me_2$), 1.78 (t, $J$ = 7 Hz, 4 H, 3- and 7-H), 2.69 (t, $J$ = 7 Hz, 4- and 6-H), 3.90 (s, 3 H, 5-$COOCH_3$), and 6.34 (s, 1 H, 10-H). |
| 1.14 (s, 6 H, C$Me_2$), 1.57 and 2.82 (each t, $J$ = 7 Hz, each 2 H, 3- and 4-H), 3.57 and 3.74 (each s, each 3 H, 7-$OCH_3$ and 5-$COOCH_3$), 6.39 and 6.94 (each d, $J$ = 2.5 Hz, each 1 H, 8- and 6-H). |
| 1.35 (s, 6 H, C$Me_2$), 1.75 (t, $J$ = 7 Hz, 4 H, 3- and 7-H), 2.71 (t, $J$ = 7 Hz, 4 H, 4- and 6-H), 3.84 (s, 3 H, 5-$COOCH_3$), and 5.39 (s, 1 H, exchanged with $D_2O$, 10-OH). |

*Table 1 (continued)*

| Compound | Yield[a] [%] | M.p. [°C] | Molecular formula[k] |
|---|---|---|---|
| **9a** | 92 | oil | $C_{15}H_{20}O_5$ |
| **10a** | 95[g] | 101–102 | $C_{18}H_{24}O_5$ |
| **11a** | 80[g] | 155–156 | $C_{18}H_{24}O_5$ |
| **12** | 80[f] (1:9) | 65–66 | $C_{14}H_{16}O_4$ |
| **13** | 85 (1:4) | oil | $C_{14}H_{16}O_4$ |
| **14** | 90 (1:4) | oil | $C_{15}H_{18}O_5$ |
| **15** | 90 (1:9) | oil | $C_{14}H_{16}O_4$ |

[a] Values in parentheses given after the yield are the ratio of benzene—petroleum ether used as eluant.

[b] Mixture of **2** + **3** + **4** separated by column chromatography on silica gel, eluting with benzene—petroleum ether (7:3) for **2**, benzene for **3** and benzene—ethyl acetate (19:1) for **4**.

[c] Mixture of **5** + **6** + **7** separated by column chromatography, eluting with benzene—petroleum ether (3:2) for **5**, benzene—petroleum ether (4:1) for **6** and benzene—ethyl acetate (9:1) for **7**.

[d] Mixture of **8** + **9** separated by column chromatography, eluting with benzene—ethyl acetate (9:1) for **8** and benzene—ethyl acetate (4:1) for **9**.

[e] Mixture of **10** + **11** separated by column chromatography, eluting with

| $^1$H-NMR chemical shift, ($\delta$/ppm, $J$ in Hz) |
|---|
| 1.39 (s, 6 H, C$Me_2$), 1.84 and 2.78 (each t, $J = 7$ Hz, each 2 H, 3- and 4-H), 3.87 and 3.90 (each s, 6 H, 3 H, 7-$OCH_3$, 8-$OCH_3$ and 5-$COOCH_3$), and 7.38 (s, 1 H, 6-H). |
| 1.30 (s, 12 H, 2 × C$Me_2$), 1.60–1.84 (m, 4 H, 3- and 9-H), 2.40–2.70 (m, 4 H, 4- and 10-H), 3.82 (s, 3 H, 6-$COOCH_3$), and 12.16 (s, 1 H, exchanged with $D_2O$, 5-OH). |
| 1.33 (s, 12 H, 2 × C$Me_2$), 1.75 (t, $J = 7$ Hz, 4 H, 3- and 7-H), 2.71 (t, $J = 7$ Hz, 4 H, 4- and 6-H), 3.83 (s, 3 H, 10-$COOCH_3$), and 5.49 (s, 1 H, exchanged with $D_2O$, 5-OH). |
| 1.36 (s, 6 H, C$Me_2$), 3.73 and 3.86 (each s, each 3 H, 6-$OCH_3$ and 5-$COOCH_3$), 5.60 and 6.21 (each d, $J = 10$ Hz, each 1 H, 3- and 4-H), 6.58 and 6.70 (each d, $J = 9$ Hz, each 1 H, 7- and 8-H). |
| 1.30 (s, 6 H, C$Me_2$), 3.66 and 3.75 (each s, each 3 H, 7-$OCH_3$ and 5-$COOCH_3$), 5.55 (d, $J = 10$ Hz, 1 H, 3-H), 6.49 and 6.95 (each d, $J = 2.5$ Hz, each 1 H, 8- and 6-H), and 7.10 (d, $J = 10$ Hz, 1 H, 4-H). |
| 1.50 (s, 6 H, C$Me_2$), 3.89 and 3.92 (each s, 6 H, and 3 H, 7-$OCH_3$, 8-$OCH_3$ and 5-$COOCH_3$), 5.60 and 6.30 (each d, $J = 10$ Hz, each 1 H, 3- and 4-H), and 7.29 (s, 1 H, 6-H). |
| 1.34 (s, 6 H, C$Me_2$), 3.63 and 3.74 (each s, each 3 H, 6-$OCH_3$ and 8-$COOCH_3$), 5.60 and 6.18 (each d, $J = 10$ Hz, each 1 H, 3- and 4-H), 6.60 and 7.06 (each d, $J = 2.5$ Hz, each 1 H, 5- and 7-H). |

benzene—petroleum ether (7:3) for **10** and benzene—ethyl acetate (19:1) for **11**.

[f–h] Solvents for recrystallisation: [f] petroleum ether; [g] benzene; [h] ethyl acetate—benzene.

[i] $CDCl_3 + CF_3COOH$.

[j] *DMSO-$d_6$*.

[k] The analytical data (C, H) are in full agreement with the molecular formulas.

*Dehydrogenation of Methyl 6-Methoxy-2,2-dimethyl-3,4-dihydro-2H-1-benzopyran-5-carboxylate* (**3a**) *with DDQ*

*General Procedure*

**3a** (0.1 g, 0.4 mmol) in dry benzene (15.0 ml) was refluxed for 50 h with *DDQ* (0.1 g, 0.4 mmol). The solution was filtered, the filtrate distilled and the residue thus obtained was purified by column chromatography and the column eluted with benzene—petroleum ether (1:9) to give **12** as colourless needles (0.08 g), m.p. 65–66 °C. For other products see Table 1.

## References


1 *Yoshihiko O., Hiromichi M., Katsura M.*, Agric. Biol. Chem. **40**, 1245 (1976).
2 *Delle Monache F., Delle Monache G., Marini Bettolo G. B., Fernandes De Albuquerque M. M., Francisco De Mello J., Goncalves De Lima O.*, Gazz. Chim. Ital. **106**, 935 (1976).
3 *Haller H. L.*, J. Amer. Chem. Soc. **53**, 733 (1931).
4 *Baudrenghien J., Jadot J., Huls R.*, Bull. Cl. Sci. Acad. Roy. Belg. **39**, 105 (1953).
5 *Stamm O. A., Schmid H., Buchi J.*, Helv. Chim. Acta **41**, 2006 (1958).
6 *Schwarz J. S. P., Cohien A. I., Ollis W. D., Kaczoa E. A., Jackman L. M.*, Tetrahedron **20**, 1317 (1964); **20**, 1331 (1964).
7 *Delle Monache F., Delle Monache G., Marini Bettolo G. B., Fernandes De Albuquerque M. M., Francisco De Mello J., Goncalves De Lima O.*, Gazz. Chim. Ital. **107**, 189 (1977).
8 *Mukerjee S. K., Sarkar S. C., Seshadri T. R.*, Tetrahedron **25**, 1063 (1969).
9 *East A. J., Ollis W. D., Wheeler R. F.*, J. Chem. Soc. (C) **1969**, 365.
10 *Delle Monache F., Marletti F., Marini Bettolo G. B., Francisco De Mello J., Goncalves De Lima O.*, Lloydia **40**, 201 (1977).
11 *Lee H. H.*, J. Chem. Soc. Perkin Trans. I **1981**, 3205.
12 *Nickl J.*, Chem. Ber. **91**, 1372 (1958).
13 *Chatterjee J. N., Banerji K. D., Prasad N.*, Chem. Ber. **96**, 2356 (1963).
14 *Nickl J.*, Chem. Ber. **92**, 1989 (1959).
15 *Ahluwalia V. K., Arora K. K.*, Tetrahedron **37**, 1437 (1981).
16 *Ahluwalia V. K., Jolly R. S., Tehim A. K.*, Tetrahedron, in press.
17 *Ahluwalia V. K., Khanna M., Singh R. P.*, Monatsh. Chem., in press.
18 *Marta M., Marini Bettolo G. B., Delle Monache F., Lupi A.*, Farmaco, Ed. Sci. **36**, 794 (1981).