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# A Convenient Synthesis of Linear 2-Methylpyranochromones

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A convenient synthesis of linear 2-methylpyranochromones, *viz.*, spatheliachromen(5-hydroxy-2,2,8-trimethyl-2*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-6-one), *O*-methylspatheliachromen (5-methoxy-2,2,8-trimethyl-2*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-6-one) (**8**) and *O*-methylallopteroxylin (5-methoxy-2,8,8-trimethyl-4*H*,8*H*-benzo[1,2-*b*:3,4-*b'*]dipyran-4-one) is described by blocking the eighth position of the corresponding 7-propargyl ether derivative 7-(1,1-dimethyl-2-propynyloxy)-8-iodo-5-methoxy-2-methyl-4*H*-1-benzopyran-4-one with iodine followed by thermal cyclization. The linear pyranochromones 2,2,8-trimethyl-2*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-6-one and **8** are also synthesized starting with the easily available appropriate 3,4-dihydro-2,2-dimethyl-2*H*-1-benzopyran-7-ols following the steps of Claisen condensation with ethyl acetate, cyclization with ethanolic sulfuric acid followed by dehydrogenation with NBS.

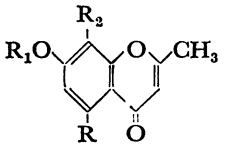
The occurrence[1] of 2-methyl linear pyranochromones, *viz.*, spatheliachromen prompted us to devise a convenient method for their synthesis. A few syntheses of these chromones are known[2,3] but these involve a number of steps and the overall yield is poor.

Attempts have now been made for the synthesis of linear pyranochromones by using our earlier finding[4] that if position-8 of a coumarin ring is blocked by an iodo group, the cyclization of the corresponding 7-propargyl ethers of 2*H*-1-benzopyran-2-ones (coumarins) on heating with *N,N*-dimethylaniline gives rise to linear pyranocoumarins, cyclization taking place at position 6 with simultaneous removal of iodine. As a test case 7-hydroxy-2-methyl-4*H*-1-benzopyran-4-one[5] (**1**) was used. Its iodination with iodine and periodic acid gave 7-hydroxy-8-iodo-2-methyl-4*H*-1-benzopyran-4-one[6] (**2**), which on propargylation with 3-chloro-3-methyl-1-butyne gave 7-(1,1-dimethyl-2-propynyloxy)-8-iodo-2-methyl-4*H*-1-benzopyran-4-one (**3**). Compound **3** on heating with *N,N*-dimethylaniline gave a mixture of two products which were separated by preparative TLC. The lower band on elution gave the linear product *i.e.* 2,2,8-trimethyl-2*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-6-one (**4**). Its structure was assigned on the basis of $^1$H NMR spectral data which showed besides other signals, two singlets at $\delta$ 6.65 and 7.65 for the two para aromatic protons. The upper band on elution gave the angular pyranochromone, *viz.*, 2,8,8-trimethyl-4*H*,8*H*-benzo[1,2-*b*:3,4-*b'*]dipyran-4-one (**5**). Its structure was assigned on the basis of its $^1$H NMR spectral data which showed two doublets at $\delta$ 6.89 and 8.00 ($J$=10 Hz each) for two ortho-coupled aromatic protons. It was also found to be identical (mp, mixed mp, superimposed IR) with an authentic sample[1] prepared by cyclization of 7-(1,1-dimethyl-2-propynyloxy)-2-methyl-4*H*-1-benzopyran-4-one (**6**).

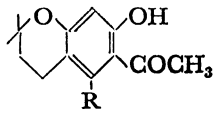
Using the above method, spatheliachromen (**7**) and *O*-methylspatheliachromen (**8**) have now been synthesized starting from 7-(1,1-dimethyl-2-propynyloxy)-8-iodo-5-methoxy-2-methyl-4*H*-1-benzopyran-4-one (**9**), which was prepared as follows: 2-Hydroxy-4-benzyloxy-6-methoxyacetophenone[7] on Claisen condensation with ethyl acetate in the presence of pulverized sodium followed by the cyclodehydration with concd sulfuric acid in ethanol gave 7-benzyloxy-5-methoxy-2-methyl-4*H*-1-benzopyran-4-one (**10**). Its catalytic debenzylation afforded 7-hydroxy-5-methoxy-2-methyl-4*H*-1-benzopyran-4-one (**11**). Iodination of **11** with iodine and periodic acid gave 7-hydroxy-8-iodo-5-methoxy-2-methyl-4*H*-1-benzopyran-4-one (**12**), which on propargylation afforded **9**. Its thermal cyclization by heating with *N,N*-dimethylaniline gave a product which showed the absence of iodine indicating that iodine was knocked out in the above reaction. It was found to be a mixture of three products. The slowest moving band on elution gave a product which gave a green iron(III) chloride reaction indicating that the 5-hydroxyl was free. It gave positive Gibbs' test, indicating that the para position to the hydroxyl group was free. On the basis of this, it was assigned the linear chromone structure, *viz.*, 5-hydroxy-2,2,8-trimethyl-2*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-6-one (**7**). It was identical in mp and $^1$H NMR spectral data with spatheliachromen isolated from *Spathelia sorbifolia*.[1] The middle band on elution gave a product, which was identical with the product obtained by the methylation of **7**. On the basis of this, it was assigned the structure *O*-methylspatheliachromen (**8**). The upper band on elution gave a product which gave a negative iron(III) chloride reaction and Gibbs' test. On the basis of this it was assigned the angular chromone structure, *viz.*, 5-methoxy-2,8,8-trimethyl-4*H*,8*H*-benzo-[1,2-*b*:3,4-*b'*]dipyran-4-one (**13**). It was found to be identical with *O*-methylallopteroxylin isolated from *Ptaeroxylon obliquum*.[8]

In another convenient approach 6-acetyl-3,4-dihydro-2,2-dimethyl-2*H*-1-benzopyran-7-ol (**17**) (obtained[9] in one step by the reaction of isoprene with 2,4-dihydroxyacetophenone) on Claisen condensation with ethyl acetate in the presence of pulverized sodium gave 6-acetoacetyl-3,4-dihydro-2,2-dimethyl-2*H*-1-benzopyran-7-ol (**18**). Its cyclization with ethanolic sulfuric acid afforded 2,2,8-trimethyl-3,4-dihydro-2*H*,6*H*-benzo-[1,2-*b*:5,4-*b'*]dipyran-6-one (**19**). Dehydrogenation of **19** with NBS gave the required linear pyranochromone **4**, identical in all respects with the product obtained above.

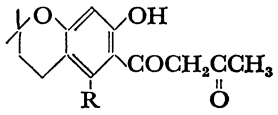
Similarly 6-acetyl-3,4-dihydro-5-methoxy-2,2-dimethyl-2*H*-1-benzopyran-7-ol (**20**) (obtained[9] by the reaction of 2,4-dihydroxy-6-methoxyacetophenone with isoprene) on Claisen condensation with ethyl acetate in the presence of pulverized sodium gave 6-acetoacetyl-3,4-dihydro-5-methoxy-2,2-dimethyl-2*H*-1-benzopyran-7-ol (**21**). Its cyclization with ethanolic sul-



| | R | $R_1$ | $R_2$ |
|---|---|---|---|
| **1** | H | H | H |
| **2** | H | H | I |
| **3** | H |  | I |
| **6** | H |  | H |
| **9** | $-OCH_3$ |  | I |
| **10** | $-OCH_3$ | $-CH_2C_6H_5$ | H |
| **11** | $-OCH_3$ | H | H |
| **12** | $-OCH_3$ | H | I |
| **15** | H | $-CH_2C_6H_5$ | H |



**17** R=H
**20** R=$OCH_3$



**18** R=H
**21** R=$OCH_3$

furic acid gave 2,2,8-trimethyl-3,4-dihydro-5-methoxy-2*H*,6*H*-benzo[1,2-*b*:5,4-*b*']dipyran-6-one (**22**). Dehydrogenation of **22** with NBS gave the required linear pyranochromone **8**, identical with the sample obtained above.

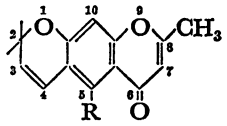
## Discussion

A synthesis of linear pyranochromones lacking an oxygen function at 5-position has not previously been available. Blocking the more reactive 8-position by iodine represents the potential route for achieving the same. In the preparation of linear pyranochromones the thermal cyclization of **3** and **9** gives a mixture of the linear and the angular pyranochromones. It shows that the reaction is nonregiospecific, as compared to the thermal cyclization in coumarins[4] which is regiospecific. A possible explanation for the nonregiospecificity in the case of chromones is due to more fixation of double bonds as compared to that of coumarins. It is believed that in this case, the loss of iodine and its cyclization are competing reactions. All attempts to make the above cyclization regiospecific, using a variety of conditions, are unsuccessful.

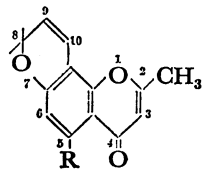
The alternate route employed for the synthesis of linear pyranochromones involving the use of the corresponding 3,4-dihydro-2*H*,6*H*-benzo[1,2-*b*:5,4-*b*']-dipyran-6-ones (**17** and **20**) is more convenient.

## Experimental

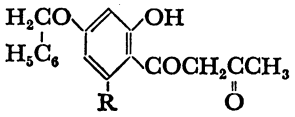
Melting points are uncorrected. The NMR spectra were recorded on Perkin Elmer R-32 instrument with TMS as an internal standard.



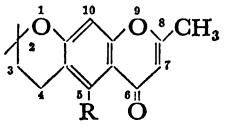
**4** R=H
**7** R=OH
**8** R=$OCH_3$



**5** R=H
**13** R=$OCH_3$



**14** R=H
**16** R=$OCH_3$



**19** R=H
**22** R=$OCH_3$

*2,2,8-Trimethyl-2*H,*6*H-*benzo[1,2*-b:*5,4*-b']*dipyran-6-one* (**4**) *1-(4-Benzyloxy-2-hydroxyphenyl)-1,3-butanedione* (**14**): A solution of 4-benzyloxy-2-hydroxyacetophenone[8] (1 g, 4.1 mmol) in dry ethyl acetate (5 ml) was added to pulverized sodium (0.5 g), the mixture being shaken and cooled. After the initial vigorous reaction had subsided, the reaction mixture was heated in a boiling water bath for 3 h. The mixture was cooled, diluted with water and extracted with ether to remove excess of ethyl acetate. The clear alkaline solution was acidified in cold with dilute acetic acid when yellow solid separated. It crystallized from benzene–petroleum ether as shining needles of **14** (0.6 g, 1.75 mmol) (46%) mp 120—121 °C. Found: C, 71.8; H, 5.7%. Calcd for $C_{17}H_{16}O_4$: C, 71.9; H, 5.6%. $^1$H NMR($CDCl_3$) $\delta$=2.12 (s, $CH_3$ of enol); 2.30(s, $CH_3$ of keto); 4.02(s, $-\underset{\underset{O}{\|}}{C}-\underline{CH_2}-\underset{\underset{O}{\|}}{C}-$ of keto) 5.10(s, 2H, $-O\underline{CH_2}C_6H_5$); 6.08(s, $-\underset{\underset{OH}{|}}{CH}=C-$ of enol); 6.55(m, 2H, H3 and H5); 7.45(s, 5H, $-OCH_2C_6\underline{H_5}$); 7.60 (d, $J$=10 Hz, 1H, H6); 12.50(s, 1H, –OH exchangeable with $D_2O$). The integration of the spectrum showed that the ratio of keto-enol forms is 1:2.

*7-Benzyloxy-2-methyl-4*H-*1-benzopyran-4-one* (**15**): **14** (0.2 g, 0.64 mmol) in absolute ethanol (15 ml) containing concd sulfuric acid (few drops) was refluxed for 20 min on a water bath. The mixture was cooled, diluted with water (30 ml) and rendered alkaline by adding few drops of sodium hydroxide solution (5%). The separated solid was filtered and crystallized from methanol as cream-colored crystals of **15** (0.15 g; 0.67 mmol) (88%) mp 115—116 °C. Found: C, 76.8; H, 5.3%. Calcd for $C_{17}H_{14}O_3$: C, 76.7; H, 5.3%. $^1$H NMR($CDCl_3$) $\delta$=2.29(s, 3H, $CH_3$); 5.05(s, 2H,

$-OCH_2C_6H_5$); 6.02(s, 1H, H3); 6.90(m, 2H, H6 and H8); 7.25(s, 5H, $-OCH_2C_6H_5$); 7.95(d, $J$=10 Hz, 1H, H5).

*7-Hydroxy-2-methyl-4H-1-benzopyran-4-one (1)*: Palladium charcoal (0.5 g, 5%) in ethyl acetate (30 ml) was saturated with hydrogen gas with stirring. A solution of the above chromone **15** (0.5 g) in ethyl acetate (40 ml) was then added and hydrogenation continued till the rapid absorption ceased. The reaction mixture was freed from catalyst by filtration and solvent distilled to give required product **1** (0.2 g; 1.14 mmol) (60.6%) mp 254—255 °C (lit,[5] 254—255 °C).

*7-Hydroxy-8-iodo-2-methyl-4H-1-benzopyran-4-one (2)*: It was prepared following the method described in literature.[6]

*7-(1,1-Dimethyl-2-propynyloxy)-8-iodo-2-methyl-4H-1-benzopyran-4-one (3)*: A solution of **2** (1 g, 3.90 mmol) in dry acetone (175 ml) was refluxed with 3-chloro-3-methyl-1-butyne (4 ml, 39.2 mmol) in the presence of anhydrous potassium carbonate (3 g) and anhydrous potassium iodide (1.9 g) for 24 h. The solvent was distilled off and the residue treated with ice. The separated solid was filtered, washed with a dilute solution of sodium carbonate and water and crystallized from benzene–petroleum ether to give **3** (0.65 g, 2.14 mmol) (54%) as colorless needles mp 144—145 °C. Found: C, 56.1; H, 4.2%. Calcd for $C_{15}H_{13}O_3I$: C, 56.0; H, 4.0%. $^1$H NMR($CDCl_3$) $\delta$=1.75(s, 6H, $C(CH_3)_2$); 2.40 (s, 3H, $CH_3$); 2.62(s, 1H, C≡CH); 6.05(s, 1H, H3); 7.54 (d, $J$=10 Hz, 1H, H6); 8.00(d, $J$=10 Hz, 1H, H5).

*2,2,8-Trimethyl-2H,6H-benzo[1,2-b:5,4-b']dipyran-6-one (4)*: The above 1,1-dimethyl-2-propynyl ether (**3**) (0.5 g, 1.65 mmol), was refluxed with *N,N*-dimethylaniline (3 ml) for 12 h. The cooled reaction mixture was poured over ice cold hydrochloric acid. The solution was extracted thrice with ethyl acetate (150 ml); washed with 5% HCl, 5% NaOH, and finally with water and dried ($Na_2SO_4$). Distillation of ethyl acetate yielded a mixture of two products, which were separated by preparative TLC (benzene–acetone, 9:1). Elution of lower band with ether yielded **4** which crystallized from benzene–petroleum ether to give shining white crystals (0.15 g, 0.61 mmol) (38%) mp 163—164 °C. Found: C, 74.5; H, 5.8%. Calcd for $C_{15}H_{14}O_3$: C, 74.3; H, 5.79%. $^1$H NMR($CDCl_3$) $\delta$=1.45(s, 6H, $C(CH_3)_2$); 2.35(s, 3H, $CH_3$); 5.65(d, $J$=10 Hz, 1H, H4); 6.00(s, 1H, H7); 6.35(d, $J$=10 Hz, 1H, H3); 6.65(s, 1H, H10); 7.65 (s, 1H, H5). The compound **4** is identical (mp, mixed mp, superimposed IR) with the sample obtained below.

The upper band on elution with ether gave a product which was crystallized from benzene–petroleum ether to give colorless needles of 2,8,8-trimethyl-4*H*,8*H*-benzo[1,2-*b*:3,4-*b'*]dipyran-4-one (**5**) (0.25 g, 1.0 mmol) (64%) mp 130—131 °C (lit,[10] mp 130—132 °C). Found: C, 74.2; H, 5.6%. Calcd for $C_{15}H_{14}O_3$: C, 74.3; H, 5.79%. $^1$H NMR($CDCl_3$) $\delta$=1.45(s, 6H, $C(CH_3)_2$); 2.35(s, 3H, $CH_3$); 5.70(d, $J$=10 Hz, 1H, H10); 6.05(s, 1H, H3); 6.89(m, 2H, H6 and H9); 8.00(d, $J$=10 Hz, 1H, H5).

*2,2,8-Trimethyl-2H,6H-benzo[1,2-b:5,4-b']dipyran-6-one (4)*. *6-Acetoacetyl-3,4-dihydro-2,2-dimethyl-2H-1-benzopyran-7-ol (18)*: 6-Acetyl-3,4-dihydro-2,2-dimethyl-2*H*-1-benzopyran-7-ol[9] (**17**), (1 g, 4.5 mmol) dissolved in dry ethyl acetate (20 ml) was treated with pulverized sodium (0.5 g). The mixture was refluxed on a boiling water bath for 4 h, cooled and treated with crushed ice very slowly. The brownish alkaline layer was separated and extracted with ether to remove excess of ethyl acetate and unreacted ketone. Acidification of cold alkaline solution with dilute acetic acid (10%) gave a white solid. It was crystallized from benzene–petroleum ether (0.75 g, 2.8 mmol) (75%) mp 108—109 °C. Found: C, 68.5; H, 6.8%. Calcd for $C_{15}H_{18}O_4$: C, 68.7; H, 6.9%). $^1$H NMR ($CDCl_3$) $\delta$=1.31(s, 6H, $C(CH_3)_2$); 1.75 and 2.70 (t, each, $J$=7 Hz, 2H each, H3 and H4); 2.05(s, $CH_3$ of enol); 2.25(s, $CH_3$ of keto); 3.95(s, $-\overset{\overset{O}{\|}}{C}-\underline{CH_2}-\overset{\overset{O}{\|}}{C}-$ of keto); 5.98(s, $-CH=\underset{\underset{OH}{|}}{C}-$ of enol); 6.28(s, 1H, H8); 7.30(s, 1H, H5); 13.8(s, 1H, –OH exchangeable with $D_2O$). The integration of the spectrum showed that the ratio of keto-enol is 1:2.

*2,2,8-Trimethyl-3,4-dihydro-2H,6H-benzo[1,2-b:5,4-b']dipyran-6-one (19)*: The diketone **18** (0.2 g, 0.76 mmol) in absolute ethanol (25 ml) containing concd sulfuric acid (2 ml) was refluxed for 2 h on a boiling water bath. The mixture was cooled, diluted with water (25 ml) and rendered alkaline with aq sodium hydroxide. The separated solid was filtered and crystallized from ethanol as pale yellow needles of **19** (75%) (0.15 g, 0.61 mmol), mp 149—150 °C. Found: C, 74.3; H, 6.4%. Calcd for $C_{15}H_{16}O_3$: C, 74.4; H, 6.8%. $^1$H NMR($CDCl_3$) $\delta$=1.35(s, 6H, $C(CH_3)_2$) 1.82 and 2.85(t, each, $J$=7 Hz, 2H each, H3 and H4); 2.32(s, 3H, $CH_3$); 6.01(s, 1H, H7); 6.7(s, 1H, H10), 7.86(s, 1H, H5).

*2,2,8-Trimethyl-2H,6H-benzo[1,2-b:5,4-b']dipyran-6-one (4)*: A solution of the chroman **19** (0.1 g, 0.41 mmol), *N*-bromosuccinimide (0.07 g) and benzoyl peroxide (0.008 g) in anhydrous carbon tetrachloride (10 ml) was refluxed for 6 h. The solution was filtered. The solvent was removed and the residue on column chromatography and elution with benzene gave **4** which crystallized from benzene–petroleum ether as light yellow needles (0.05 g, 0.20 mmol) (50%), mp and mixed mp, 163—164 °C.

*5-Hydroxy-2,2,8-trimethyl-2H,6H-benzo[1,2-b:5,4-b']dipyran-6-one (spatheliachromen) (7)*. *1-(4-Benzyloxy-2-hydroxy-6-methoxyphenyl)-1,3-butanedione (16)*: A solution of 4-benzyloxy-2-hydroxy-6-methoxyacetophenone[7] (1 g, 3.70 mmol) in dry ethyl acetate (5 ml) was added to pulverized sodium (0.5 g). The mixture was shaken and cooled. After the initial vigorous reaction had subsided, the reaction mixture was heated in a boiling water bath for 3 h. The mixture was cooled, diluted with water and extracted with ether to remove an excess of ethyl acetate. The clear brownish alkaline solution was acidified in cold with dilute acetic acid when a yellow solid separated. It crystallized from benzene–petroleum ether as pale yellow shining needles of **16** (0.6 g, 1.89 mmol) (52%), mp 135—136 °C. Found: C, 68.9; H, 5.7%. Calcd for $C_{18}H_{18}O_5$: C, 68.7; H, 5.9%. $^1$H NMR($CDCl_3$) $\delta$=2.08(s, $CH_3$ of enol); 2.15(s, $CH_3$ of keto); 3.85(s, 3H, $-OCH_3$); 3.92(s, $-\overset{\overset{O}{\|}}{C}-\underline{CH_2}-\overset{\overset{O}{\|}}{C}-$ of keto); 4.95(s, 2H, $-O\underline{CH_2}C_6H_5$); 5.85(s, $-\underline{CH}=\underset{\underset{OH}{|}}{C}-$ of enol); 6.00 and 6.15(d, each, $J$=2.5 Hz each, 2H, H3 and H5); 7.35 (s, 5H, $-OCH_2C_6\underline{H_5}$); 13.50(s, –OH at C-2 of enol, exchangeable with $D_2O$); 13.80(s, –OH at C-3 of keto, exchangeable with $D_2O$). The integration of the spectrum showed that the ratio of keto and enol forms is 3:1.

*7-Benzyloxy-5-methoxy-2-methyl-4H-1-benzopyran-4-one (10)*: **16** (0.2 g, 0.63 mmol) in absolute ethanol (15 ml) containing concd sulfuric acid (few drops) were refluxed for 30 min on a water bath. The mixture was cooled, diluted with water (30 ml) and rendered alkaline by adding few drops of sodium hydroxide solution (5%). The separated solid was filtered and crystallized from methanol as colorless shining needles of **10** (0.16 g, 0.61 mmol) (80%) mp 90—91 °C. Found: C, 73.1; H, 5.3%. Calcd for $C_{18}H_{16}O_4$: C, 73.0; H, 5.4%. $^1$H NMR($CDCl_3$) $\delta$=2.20(s, 3H, $CH_3$); 3.85(s, 3H, $-OCH_3$); 5.00(s, 2H, $-O\underline{CH_2}C_6H_5$); 5.90(s, 1H, H3); 6.29 and 6.32 (d, each, $J$=2 Hz each, 1H each, H6

and H8); 7.25 (s, 5H, $-OCH_2C_6\underline{H}_5$).

*7-Hydroxy-5-methoxy-2-methyl-4H-1-benzopyran-4-one (11)*: Palladium charcoal (0.5 g, 5%) in ethyl acetate (20 ml) was saturated with hydrogen gas with stirring. A solution of the above chromone **10** (0.5 g, 1.70 mmol) in ethyl acetate (40 ml) was then added and hydrogenation continued till the rapid absorption ceased. The reaction mixture was freed from catalyst by filtration and solvent distilled to give **11** (0.2 g, 0.98 mmol) (57%) mp 215—216 °C. Found: C, 64.2; H, 4.9%. Calcd for $C_{11}H_{10}O_4$: C, 64.0; H, 4.85%.

Its acetate (prepared by acetic anhydride–pyridine) melted at 114—115 °C. $^1$H NMR($CDCl_3$) $\delta$=2.32(s, 3H, $CH_3$); 2.38(s, 3H, $-COCH_3$); 3.95(s, 3H, $-OCH_3$); 6.08(s, 1H, H3); 6.55 and 6.82(d, each, $J$=2.5 Hz each, 1H each, H5 and H8).

*7-Hydroxy-8-iodo-6-methoxy-2-methyl-4H-1-benzopyran-4-one (12)*: **11** (2 g, 6.80 mmol) was dissolved in a minimum amount of ethanol and to this solution iodine (1.20 g) and periodic acid (0.38 g in water) were added. The mixture was stirred for 2 h at a room-temperature and then diluted with water to give chromone **12** (2.5 g, 8.75 mmol) (89%). It crystallized from ethanol as light yellowish needles, mp 225—226 °C. Found: C, 46.5; H, 3.10%. Calcd for $C_{11}H_9O_4I$: C, 46.3; H, 3.15%.

Its acetate (prepared by acetic anhydride–pyridine) melted at 145—146 °C. $^1$H NMR($CDCl_3$) $\delta$=2.39(s, 3H, $CH_3$); 2.43(s, 3H, $-COCH_3$); 3.95(s, 3H, $-OCH_3$); 6.10(s, 1H, H3); 6.65(s, 1H, H6).

*7-(1,1-Dimethyl-2-propynyloxy)-8-iodo-5-methoxy-2-methyl-4H-1-benzopyran-4-one (9)*: A solution of **12** (1 g, 3.50 mmol) in dry acetone (200 ml) was refluxed with 3-chloro-2-methyl-1-butyne (4 ml, 38.9 mmol) in the presence of anhydrous potassium carbonate (3 g) and anhydrous potassium iodide (1.5 g) for 24 h. Working up of the reaction mixture yielded **9** (0.7 g, 1.99 mmol) (58.3%) which crystallized from benzene–petroleum ether as white needles mp 185—186 °C. Found: C, 54.8; H, 4.30%. Calcd for $C_{16}H_{15}O_4I$: C, 54.7; H, 4.27%. $^1$H NMR($CDCl_3$) $\delta$=1.80(s, 6H, $C(CH_3)_2$); 2.25(s, 3H, $CH_3$); 2.70(s, 1H, C≡CH); 3.90(s, 3H, $-OCH_3$); 6.00(s, 1H, H3); 7.29(s, 1H, H6).

*5-Hydroxy-2,2,8-trimethyl-2H,6H-benzo[1,2-b:5,4-b']dipyran-6-one (Spatheliachromen) (7)*: The above 1,1-dimethyl-2-propynyl ether (**9**) (0.5 g, 0.7 mmol) was refluxed with *N,N*-dimethylaniline (3 ml) for 12 h. The cooled reaction mixture was poured over ice cold hydrochloric acid and worked up (as in case of **4**) to yield a mixture of three products, which were separated by preparative TLC. The slowest moving band on elution with ether gave **7**. It crystallized from ethyl acetate–petroleum ether to give colorless needles (0.100 g, 0.39 mmol) (27%), mp 139—140 °C (lit,[1] mp 139—140 °C). Found: C, 70.0; H, 5.60%. Calcd for $C_{15}H_{14}O_4$: C, 69.75; H, 5.50%. $^1$H NMR($CDCl_3$) $\delta$=1.45 (s, 6H, $C(CH_3)_2$); 2.32(s, 3H, $CH_3$) 5.60(d, $J$=10 Hz, 1H, H4); 6.01(s, 1H, H7); 6.28(s, 1H, H10); 6.71(d, $J$= 10 Hz, 1H, H3); 13.06(s, 1H, –OH, exchangeable with $D_2O$).

The middle band on elution gave a product which was assigned the structure *O*-methylspatheliachromen (**8**). It crystallized from benzene–petroleum ether (0.150 g, 0.455 mmol) (37.5%), mp 121—122 °C (lit,[1] mp 120—122 °C). Found: C, 70.35; H, 6.0%. Calcd for $C_{16}H_{16}O_4$: C, 70.6; H, 5.9%). $^1$H NMR($CDCl_3$) $\delta$=1.47(s, 6H, $C(CH_3)_2$); 2.28 (s, 3H, $CH_3$); 3.90(s, 3H, $-OCH_3$); 5.71(d, $J$=10 Hz, 1H, H4); 6.00(s, 1H, H7); 6.58(s, 1H, H10) and 6.75(d, 1H, $J$=10 Hz, H3). The compound **8** was identical (mp, mixed mp, superimposed IR) with the sample obtained below.

The upper most band on elution with ether gave a solid product which was crystallized from benzene–petroleum ether to give *O*-methylallopteroxylin (**13**) (0.100 g; 0.39 mmol) (25%) mp 152—154 °C (lit,[8] mp 150—152 °C). Found: C, 70.35; H, 6.09%. Calcd for $C_{16}H_{16}O_4$: C, 70.6; H, 5.9%. $^1$H NMR($CDCl_3$) $\delta$=1.48(s, 6H, $C(CH_3)_2$); 2.29 (s, 3H, $CH_3$); 3.93(s, 3H, $-OCH_3$); 5.56(d, $J$=10 Hz, 1H, H10); 6.01(s, 1H, H3); 6.31(s, 1H, H6) and 6.71(d, $J$= 10 Hz, 1H, H9).

*5-Methoxy-2,2,8-trimethyl-2H,6H-benzo[1,2-b:5,4-b']dipyran-6-one (8)*. *6-Acetoacetyl-3,4-dihydro-5-methoxy-2,2-dimethyl-2H-1-benzopyran-7-ol (21)*: 6-Acetyl-3,4-dihydro-5-methoxy-2,2-dimethyl-2*H*-1-benzopyran-7-ol[9] (**20**) (0.5 g, 2.0 mmol) dissolved in dry ethyl acetate (10 ml) was treated with pulverized sodium (0.25 g). The mixture was refluxed on a boiling water bath for 4 h. The reaction mixture was worked up as usual and the solid obtained was crystallized from benzene–petroleum ether as pale yellow needles (0.35 g, 1.2 mmol) (70%) mp 104—105 °C. Found: C, 60.2; H, 7.91%. Calcd for $C_{16}H_{20}O_5$: C, 60.23; H, 7.94%. $^1$H NMR($CDCl_3$) $\delta$=1.34(s, 6H, $C(CH_3)_2$), 1.75 and 2.7(t, each, $J$=7 Hz, each 2H, H3, and H4); 2.13(s, $CH_3$ of enol); 2.22(s, $CH_3$ of keto), 3.75(s, 3H, $OCH_3$), 4.02(s, $-\underset{\underset{O}{\|}}{C}-\underline{CH}-\underset{\underset{O}{\|}}{C}-$ of keto); 5.86(s, $-CH=\underset{\underset{OH}{|}}{C}-$); 6.1(s, 1H, H8); 13.7(s, 1H, –OH exchangeable with $D_2O$). The integration of the spectrum showed that the ratio of keto and enol is 1:2.

*5-Methoxy-2,2,8-trimethyl-3,4-dihydro-2H,6H-benzo[1,2-b:5,4-b']dipyran-6-one (22)*: The diketone **21** (0.2 g, 0.68 mmol) in ethanol (25 ml) containing concd sulfuric acid (2 ml) was refluxed for 2 h on a boiling water bath. Working up of the reaction mixture as in the case of **19** gave **22** which crystallized from ethanol as yellow needles (0.15 g, 0.55 mmol) (75%) mp 114—115 °C. Found: C, 70.54; H, 6.52%. Calcd for $C_{16}H_{18}O_4$: C, 70.59; H, 6.57%. $^1$H NMR($CDCl_3$) $\delta$=1.34(s, 6H, $C(CH_3)_2$), 1.78 and 2.76(t, each, $J$=7 Hz, 2H each H3, and H4), 2.23(s, 3H, $CH_3$); 3.81 (s, 3H, $-OCH_3$); 5.85(s, 1H, H7); 6.44(s, 1H, H10).

*5-Methoxy-2,2,8-trimethyl-2H,6H-benzo[1,2-b:5,4-b']dipyran-6-one (8)*: Dehydrogenation of **22** (0.1 g, 0.36 mmol) with NBS as in the case of **4** gave **8** (0.06 g, 0.22 mmol) (60%) mp 120—121 °C.

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