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BY

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SOME NATURALLY OCCURRING DIMETHYLCHROMENES

PART I.—THE CHROMENES OF *MEDICOSMA CUNNINGHAMII* Hook

MAURICE D. SUTHERLAND, M.SC., A.A.C.I.

Summary

The leaves of *Medicosma cunninghamii* Hook yield on steam distillation, an essential oil from which two dimethylchromene derivatives have been isolated. One is a previously unknown yellow crystalline phenol which is proved to be 7-hydroxy-5-methoxy-8-acetyl-2 : 2-dimethylchromene (I, R = R′ = H) and is therefore named *allo*evodionol. The second substance is 5 : 7-dimethoxy-6-acetyl-2 : 2-dimethylchromene (II, R = CH_3, R′ = H) the methyl ether of evodionol (1). The substance "$C_{16}H_{20}0_4$" m.p. 107°, isolated by Jones and Wright (2) from *Evodia elleryana*, is shown to be actually $C_{15}H_{18}0_4$, being the methyl ether of *allo*evodionol (I, R = CH_3, R′ = H).

Steam distillation of the leaves of *Medicosma cunninghamii* Hook, a rutaceous tree which grows in Queensland and New South Wales, yields an essential oil which is at present being examined, and in addition yields water insoluble substances of high boiling point which are not terpene derivatives. Two crystalline substances have been separated by fractional crystallization from this source, and it is possible that the oily mother liquors of these will yield other related chemical entities. The principal substance is a yellow ketonic phenol of m.p. 71°-72°, the other being a colourless ketone of m.p. 78°-78.5° present in smaller proportion.

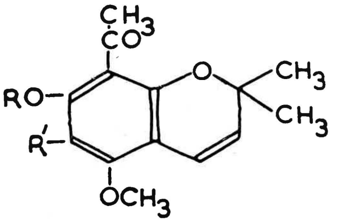
The yellow *phenol* for which the name *allo*evodionol is proposed, has the molecular formula $C_{14}H_{16}0_4$, and contains one phenolic group which gives rise to a dark green ferric reaction. It readily forms a colourless *acetate* m.p. 74°-75° and a colourless *methyl ether* m.p. 106.5°-107° (*benzylidene derivative* m.p. 164°-165°). A ketonic group results in the formation of a 2 : 4-*dinitrophenylhydrazone* m.p. 194-195°; and an activated methylene group is indicated by the formation of a red *benzylidene derivative* m.p. 143°-143.5°, and a dark red *cinnamylidene derivative* m.p. 142.5°-143°. Hydrogenation yields an almost colourless dihydro compound m.p. 76.5°-77.5° (*benzylidene derivative* m.p. 180°-180.5°) and methoxy estimations show the presence of one such group.

Oxidation of the methyl ether by permanganate in acetone yields a *dicarboxylic acid* $C_{15}H_{18}0_8$ (III), (*dimethyl ester* m.p. 86-87°) from which it is clear that the double bond forms part of a ring. Pyrolysis of this dicarboxylic acid yields 2 : 4-dimethoxy-phloracetophenone and α-hydroxy-isobutyric acid. The close analogy between this result and the thermal decompositions reported by Lahey (3, 4) for evodionic acid obtained from methyl evodionol (II, R′ = H, R = CH_3) by oxidation, and by Wright (5) for a dibasic acid obtained from evodione

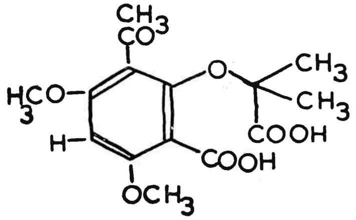
(II, R′ = R = CH_3), suggests the presence of the 2 : 2-dimethyl-chromene ring in the molecule, and accounts for the fourth oxygen atom of the molecule. This view leads to the formulation of the methyl ether as (I, R = CH_3, R′ = H) and the structure of the naturally occurring phenol is then revealed as (I, R = R′ = H) since the ortho relation of the phenolic group to the acetyl group is shown by its resistance to methylation by diazomethane and its participation in γ-pyrone formation involving the acetyl group also.

The structure suggested by the above reactions is confirmed by a comparison of certain derivatives of *allo*evodionol with the description of certain substances reported by Backhouse and Robertson (6). Thus dihydro-*allo*evodionol (m.p. 76.5°-77.5°, yellowish prisms or plates from alcohol or petroleum ether, ferric reaction brownish-red) agrees closely with 7-hydroxy-5-methoxy-8-acetyl-2 : 2-dimethylchroman (m.p. 78°, pale yellow, elongated, rectangular prisms from dilute alcohol, ferric reaction brownish-purple) prepared from 5 : 7-dihydroxy-2 : 2-dimethyl-chroman. Four other derivatives were also prepared (see Experimental), none of which differed in any significant detail from the literature description, excepting only that the melting point of 5 : 7-dimethoxy-8-β-phenylpropionyl-2 : 2-dimethylchroman, prepared by two methods from the naturally occurring phenol was found to be 63°-64° rather than the previously reported value of 74°.

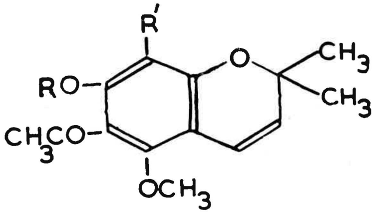
The yellow phenol is thus conclusively shown to be 7-hydroxy-5-methoxy-8-acetyl-2 : 2-dimethylchromene (I, R = R′ = H), and, considering the relation it bears to evodionol (II, R = R′ = H), the name *allo*evodionol is in accord with established precedents (7, 8).



I



III



II

The colourless crystalline ketone, m.p. 78°-78.5° was shown by analysis to be $C_{13}H_{12}(OCH_3)_2$ and was found to be identical in properties with methylevodionol (II, R = Me, R′ = H) as described by Lahey and Jones (1). The identity was confirmed by the preparation of the dinitrophenylhydrazone and the benzylidene derivative, and by mixed melting point determinations.

Jones and Wright (2) isolated a colourless substance m.p. 107°, from the essential oil of *Evodia elleryana*, distilled from leaves obtained from Mackay, Queensland, and to this compound assigned the formula $C_{13}H_{12}0_2(OCH_3)_2$. A sample of the original material gave no depression of melting point with *methyl*alloevodionol** (I, R = CH_3, R′ = H). The *benzylidene derivative* m.p. 164°-165° was prepared from both samples and proved to be identical. The substance isolated by Jones and Wright is thus actually $C_{13}H_{12}0_2(OCH_3)_2$, methyl*allo*evodionol (I, R = CH_3, R′ = H) or 5 : 7-dimethyoxy-8-acetyl-2 : 2-dimethylchromene.

The distribution of the various substituted dimethylchromenes obtained from *Evodia* species and from *M. cunninghamii* is set out in Table 1. The substance "*allo*evodione" (I, R = R' = Me) is not yet known, but it is possible that a substance $C_{13}H_{11}O_2(OCH_3)_3$ m.p. 82° isolated by Jones and Wright (2) from the essential oil of *E. elleryana* from Stradbroke Island may be actually (I, R = R' = CH_3). In support of this view it did not yield a dinitrophenylhydrazone as was found also in the case of methyl*allo*evodionol (2). The acetyl group in the *allo* series is evidently significantly more hindered than that in the evodionol series, since *allo*evodionol does not yield iodoform as does evodionol when treated under the conditions recommended by Fuson and Tullock (9) for water insoluble compounds.

Further investigations in this field are in progress.

TABLE I.

	Evodionol series II.	*allo* Evodionol series I.
R = R' = H	Evodionol *E. littoralis*	*allo*Evodionol *M. cunninghamii*
R = CH_3 R' = H	Methyl-evodionol *M. cunninghamii*	Methyl-*allo*evodionol *E. elleryana* (from Mackay only)
R = R' = CH_3	Evodione *E. elleryana* (from Stradbroke Island only)	

Experimental

The leaves of *Medicosma cunninghamii* (Hook) used in this investigation were obtained from Imbil, Queensland, some being collected by Mr. G. Lahey and Mr. L. J. Webb, Division of Plant Industry, C.S.I.R., and some by the Queensland Forestry Department.

Isolation by Steam Distillation.

The leaves steam distilled in the usual way, yielded an essential oil which formed an oily upper layer on the cloudy aqueous layer. After a few hours little more oil distilled but the aqueous layer continued to yield an oily solid (in diminishing yield) on standing even after more than eighty hours of steaming of the leaves. No completely satisfactory method was available for separating the susp material from the distillate, though some was dissolved out by passing the distillate through petrol ether and some was deposited on a seeded surface. The bulk of the material was obtained by occasionally steaming out the condenser in which considerable quantities were retained. A further quantity of the substances in question was obtained from the highest boiling fractions of the essential oil.

The dark oily semicrystalline material from the steam distillation was readily crystallized from alcohol to yield a yellow phenol m.p. 71°-72°. The mother liquors after removal of several crops of the yellow phenol deposited a mixture of yellow and colourless crystals which were separated by extraction of an ethereal solution with 10% sodium hydroxide solution followed by crystallization from ether at 0°. When almost pure the colourless substance separated satisfactorily from ethyl alcohol and the melting point was raised to 78°-78.5°.

The quantity of colourless substance obtained was about 10% of the weight of yellow phenol isolated. Some oily mother liquors remain for further examination. Owing to the partially dried state of the plant material received from Imbil and to the incompleteness of distillation and recovery, the proportion of yellow phenol in the leaves could not be satisfactorily calculated from the results of the steam distillation.

Isolation by Glycerol Codistillation.

One kilogram of finely ground air dried leaves was exhaustively extracted with ether and the residue from this extract was distilled with an excess of glycerol at gauge pressure <0.5 mm. A yellow green oil distilled with the glycerol, at first rapidly, but finally in small proportion only. The distillate was then diluted with water and a little petrol ether and on standing overnight, crystals of the yellow phenol separated in the upper layer. This material (4.77 g.) was removed by filtration and washed with water and alcohol. The mother liquor by extraction with concentrated sodium hydroxide solution yielded a mixture of phenols and acids from which a further 1.40 g. of yellow crystals was obtained, but recovery was incomplete. The combined material melted at 65-70° and after one crystallization from alcohol at 69-71°. Thus, the sample of air dried leaves contained not less than 0.62% of *allo*evodionol. Correcting for the moisture content of the ground leaves raises this figure to 0.72% of *allo*evodionol in the dry leaf.

alloEvodionol (7-Hydroxy-5-methoxy-8-acetyl-2 : 2-dimethylchromene).

This substance forms brilliant yellow crystals of rather variable form from ethyl alcohol, methyl alcohol or petrol ether, but is very soluble in acetone and chloroform. It may be distilled without decomposition at about 160° at a gauge pressure of 0.3 mm. and sublimes readily at 130° in a water pump vacuum. The melting point is 71°-72° and is depressed by admixture with evodionol. The ferric coloration in alcohol is dark green. Shaking an ethereal solution of *allo*evodionol with 10% sodium hydroxide solution yields orange crystals, probably the sodium salt of *allo*evodionol.

Analysis—Found : C, 67.4 67.9 67.9 ; H, 6.37, 6.65 6.42 ; OMe, 12.5 ; M.W., 240.

$C_{14}H_{16}O_4$ requires : C 67.73 ; H, 6.49 ; OMe, 12.5 ; M.W., 248.

The molecular weight was determined ebullioscopically using acetone in Reiche's apparatus. Unlike evodionol which required prolonged heating, *allo*evodionol demethylated quantitatively in three-quarters of an hour under the treatment described by Clark (10).

The 2 : 4-*dinitrophenyl hydrazone of alloevodionol.*

By crystallization from glacial acetic acid or ethyl acetate were formed deep red plates m.p. 194-195°.

Analysis—Found : C, 56.1 ; H, 4.63.

$C_{20}H_{20}N_4O_7$ requires : C, 56.07 ; H, 4.71.

Acetyl-alloevodionol (7-acetoxy-5-methoxy-8-acetyl-2 : 2-dimethylchromene).

*allo*Evodionol formed a yellow solution in acetic anhydride but on refluxing with anhydrous sodium acetate the colour was discharged in less than ten minutes. The reaction mixture poured into water, gave a good yield of crystalline acetyl-*allo*evodionol which could be crystallized from aqueous alcohol or from petroleum ether as colourless chunky prisms with curious blade-like projections or as sheafs of needles m.p. 74-75°.

Analysis—Found : C, 66.4 ; H, 6.14.

$C_{16}H_{18}O_5$ requires : C, 66.19 ; H, 6.25.

Benzylidene-alloevodionol (7-hydroxy-5-methoxy-8-cinnamoyl-2 : 2-dimethyl-1 : 2-chromene).

This was prepared in the manner described by Lahey (4) for the preparation of benzylidene-evodionol. The chalkone formed brilliant red needles, m.p. 143°-143.5° from alcohol and gave a red ferric coloration in alcohol.

Analysis—Found : C, 75.4 ; H, 5.98.

$C_{21}H_{20}O_4$ requires : C, 74.98 ; H, 5.99.

Cinnamylidene-alloevodionol (7 - hydroxy - 5 - methoxy - 8 - (β - styryl - acrylyl -)-2 : 2-dimethyl-1 : 2-chromene).

Cinnamic aldehyde (1 g.), *allo*evodionol (1 g.) and caustic potash (0.3 g.) were dissolved in a minimum of alcohol at room temperature. The solution darkened slowly and after two weeks sufficient water was added to cause incipient crystallization. Very dark red crystals (0.32 g.) were filtered off, washed with methyl alcohol and dried. The addition of more water to the mother liquors precipitated only yellowish material. After two crystallizations from alcohol, dark red prisms or needles, m.p. 142.5-143°, were obtained which gave a dark brown ferric coloration in alcohol.

Analysis—Found : C, 76.0 ; H, 5.98.

$C_{23}H_{22}O_4$ requires : C, 76.21 ; H, 6.12.

Dimer of alloevodionol.

From the action of dimethyl sulphate on a dioxan solution of *allo*evodionol in the presence of potassium carbonate a small quantity of a by-product was separated by virtue of its insolubility in water and ether. This yellow crystalline substance was very insoluble in cold alcohol and only slightly so in hot alcohol but crystallized from methyl ethyl ketone as yellow prisms or plates m.p. 220-221° without decomposition.

Analysis—Found : C, 68.0 ; H, 6.35 ; OMe, 12.8 ; M.W., 473.

$[C_{13}H_{13}O_3(OMe)]_2$ requires : C, 67.73 ; H, 6.49 ; OMe, 12.5 ; M.W., 496.

The molecular weight was determined ebullioscopically using acetone in Reiche's apparatus. The ferric reaction in alcohol is dark green and on shaking with hydrogen in acetone in the presence of Adams catalyst, no gas was absorbed.

Methyl-alloevodionol (5 : 7-dimethoxy-8-acetyl-2 : 2-dimethylchromene).

*allo*Evodionol (10 g.) in 10 ml. acetone was refluxed with 9 ml. of methyl iodide and 28 g. of anhydrous potassium carbonate for three days. Water was then added to dissolve the inorganic material and the upper layer after the addition of ether was worked with water and evaporated. After the addition of alcohol, the colourless crystals were filtered and washed. Two crystallizations from alcohol gave oblique plates, m.p. 106.5-107° (7.4 g.). The mother liquors yielded a further 2.0 g. of pure material. Ferric reaction negative.

Analysis—Found : C, 68.3, 68.8, 68.9 ; H, 6.80, 6.88, 6.61 ; OMe, 23.3.

$C_{13}H_{12}O_3(OMe)_2$ requires : C, 68.66 ; H, 6.91 ; OMe, 23.7.

A sample of the substance m.p. 107° isolated and described by Jones and Wright (2) from E. elleryana was available for comparison and on crystallization from alcohol gave crystals of identical appearance to those of methyl-*allo*evodionol. No depression of melting point resulted from mixing the two materials.

By the use of Brady's reagent under various conditions no crystalline dinitrophenylhydrazone could be obtained, the product being either an oil or a rather soluble orange-red amorphous solid.

Benzylidene-methyl-alloevodionol. (5 : 7-dimethoxy-8-cinnamoyl-2 : 2-dimethylchromene).

28.5 mg. of Jones and Wright's solid m.p. 107° was heated at the boiling point with 20 mg. benzaldehyde, 0.04 ml. of 10% caustic soda solution and sufficient alcohol to bring about homogenuity. A yellow colour appeared almost immediately and later yellow needles separated. After one hour's heating the solution was diluted somewhat and cooled. The crystals were filtered off and washed with water and alcohol and after drying showed m.p. 164-164.5°. Crystallization from ethyl alcohol afforded 20 mg. of yellow needles of m.p. 164-165°.

From methyl-*allo*evodionol derived from *allo*evodionol, an identical substance was obtained which caused no melting point depression on admixture.

Analysis—Found : C, 75.0 ; H, 6.26.

$C_{22}H_{22}O_4$ requires : C, 75.41 ; H, 6.33.

Dihydro-methyl-alloevodionol (5 : 7-dimethoxy-8-acetyl-2 : 2-dimethylchroman).

Methyl-*allo*evodionol (0.567 g.) was hydrogenated at room temperature in 5 ml. of absolute alcohol using Adam's catalyst (28 mg.) freshly reduced. Hydrogen (48.1 ml. = 101% of that calculated for one double bond) was absorbed in 15 minutes after which absorption ceased. The solution after filtration and concentration yielded 0.37 g. of colourless plates m.p. 81.5°-82.5°. More was obtained from the mother liquors but the chroman is rather soluble in ethyl alcohol. By crystallization from ethyl alcohol with ice cooling and from petroleum ether the melting point was raised to 82°-82.5°.

Analysis—Found : C, 68.0 ; H, 7.58.

$C_{15}H_{20}O_4$ requires : C, 68.16 ; H, 7.63.

Benzylidene-dihydro-methyl-alloevodionol (5 : 7-dimethoxy-8-cinnamonyl-2 : 2-dimethylchroman).

The alcoholic solution from the hydrogenation of 0.568 g. of methyl-*allo*evodionol was treated with an excess of benzaldehyde and 0.2 g. of caustic potash. Warmed on the waterbath for a few minutes, the solution developed a yellow colour. Dilution precipitated yellow needles which, after standing overnight, were filtered, washed with alcohol and water, and dried. Yield 0.71 g. Crystallization from alcohol raised the melting point to 132.5°-133°.

Analysis—Found : C, 75.1 ; H, 7.01.

$C_{22}H_{24}O_4$ requires : C, 74.98 ; H, 6.86.

The Oxidation of Methyl-alloevodionol to a dibasic acid (alloevodionic acid).

Methyl-*allo*evodionol (5 g.) dissolved in 200 ml. of pure dry acetone, was stirred vigorously at room temperature while 10 g. of powdered potassium permanganate was added during a period of two hours and after another hour, stirring was discontinued. Evaporation of the filtrate yielded 1.17 g. of unchanged chromene and from the manganese dioxide filter cake by repeated extraction with hot water, was obtained a solution which after concentration and acidification yielded a crystalline precipitate (3.70 g.) which was filtered, washed with water, and dried. This colourless acid was insoluble in cold solvents excepting pynidine and was recrystallized from water. When heated in a capillary from 180°, decomposition with gas evolution takes place at 193°. The temperature for instantaneous melting on a copper surface is about 235°.

Analysis—Found : C, 55.4 ; H, 5.47.

$C_{15}H_{18}O_8$ requires : C, 55.21 ; H, 5.56.

Molecular weight by titration : 333, 330 (dibasic acid).

Calculated for $C_{13}H_{16}O_4(COOH)_2$: 330.

Dimethyl ester of alloevodionic acid.

A solution of diazomethane obtained from 7.5 ml. of hydrazine hydrate was allowed to react at 0° C. with 1.35 g. of *allo*evodionic acid suspended in ether. After two days the solution was decolorized but some acid remained undissolved. This was separated by washing the ether with alkali and 0.13 g. was recovered on acidification. The ethereal solution was evaporated and the residual syrup induced to crystallize by standing with a little methyl alcohol. The mass was taken up in warm ether, crystallized on cooling at 0° C. and after a number of crystallizations from ether formed colourless prisms, m.p. 86-87° after drying in a high vacuum at 55°. Yield 0.33 g. From the mother liquors was obtained 0.70 g. of less pure material m.p. 84-86°.

Analysis—Found : C, 57.9 ; H, 6.05 ; OMe, 33.8.

$C_{17}H_{22}O_8$ requires : C, 57.62 ; H, 6.26 ; OMe, 35.0.

The Pyrolysis of alloEvodionic acid to 2 : 4-dimethoxyphenoacetophenone.

*allo*Evodionic acid (1.45 g.) was placed in a sidearm test tube in an oil bath and connected by a length of glass tubing to a trap cooled in a dry ice and acetone mixture. A water pump vacuum was applied to the system and the oil bath heated to 200° C. Decomposition began at about 190° and appeared to be almost complete in 20 minutes, after which the deep red reaction mixture was cooled and dissolved in ether. Extraction of the ether solution by sodium carbonate removed a little acidic material and the remaining solute crystallized after evaporation of the ether and trituration with alcohol. Recrystallization from alcohol yielded 0.32 g. of needles m.p. 80-81°, the ferric reaction in alcohol being deep red.

Analysis—Found : C, 61.5 ; H, 6.10.

Calculated for $C_{10}H_{12}O_4$: C, 61.21 ; H, 6.16.

No depression of melting point resulted from the addition to this pyrolysis product of authentic 2 : 4-dimethoxyacetophenone m.p. 80-81° kindly supplied by Mr. K. G. O'Brien of the Technological Museum, Sydney.

From the mother liquors a further 0.30 g. of the phenol was obtained and this by heating for eight hours at 100° with methyl iodide, potassium carbonate and acetone was converted into prisms, m.p. 101.5°-102.5° from ether and alcohol. The melting point of this substance was not depressed by mixing with an authentic sample 2 : 4 : 6-trimethoxy-acetophenone of the same melting point.

Other products resulting from the pyrolysis were (a) a colourless crystalline sublimate which formed in the connecting tube and melted in the crude state at 75°, liberated carbon dioxide from sodium bicarbonate solution and gave a yellow colour with ferric chloride solution, and (b) a small quantity of an acid of butyric odour which condensed in the dry ice trap. These are in all probability α-hydroxy-iso-butyric acid m.p. 79° and methacrylic acid.

Dihydroalloevodionol (7-Hydroxy-5-methoxy-8-acetyl-2 : 2-dimethylchroman).

*allo*Evodionol was hydrogenated in ethyl alcohol using Adams' catalyst, the product being precipitated by the addition of water. Crystallization from alcohol and hexane yielded thick rectangular plates, m.p. 76.5-77.5° with a faint yellowish tinge, which gave a brownish red ferric reaction in alcohol.

Analysis—Found : C, 67.5 ; H, 7.20.

Calculated for $C_{14}H_{18}O_4$: C, 67.18 ; H, 7.25.

For this compound Backhouse and Robertson (6) found m.p. 78° and ferric reaction brownish purple.

Benzylidene-dihydro-alloevodionol (7-hydroxy-5-methoxy-8-cinnamoyl-2 : 2-dimethylchroman).

Dihydro-*allo*evodionol (1 g.) and 0.25 g. of sodium hydroxide were dissolved in the minimum quantity of alcohol and 1.3 ml. of benzaldehyde added. Crystals (1.15 g.) of m.p. 179.5-180° separated overnight and after five days were filtered, washed, and dried. Crystallization from alcohol or methyl ethyl ketone yielded orange needles m.p. 180°-180.5°.

Analysis—Found : C, 74.1 ; H, 6.50.

$C_{21}H_{22}O_4$ requires : C, 74.53 ; H, 6.55.

7-*Hydroxy*-6-*methoxy*-8-β-*phenylpropionyl*-2 : 2-*dimethylchroman*.

Benzylidene-dihydro*allo*evodionol was hydrogenated in alcohol using Adams' catalyst until absorption was complete. The filtrate from the catalyst readily deposited colourless plates which were crystallized from ethyl and methyl alcohols to constant melting point 103-104°.

Backhouse and Robertson (6) give m.p. 104° for this compound prepared by the methylation of 5 : 7-dihyroxy-8-β-phenylpropionyl-2 : 2-dimethylchroman.

5 : 7-*Dimethoxy*-8-β-*phenylpropionyl*-2 : 2-*dimethylchroman*.

Benzylidene-methyl-*allo*evodionol (370 mg.) treated with hydrogen and a pallodium charcoal catalyst in alcohol solution took up 1.86 moles of hydrogen in 55 minutes yielding a colourless solution which was evaporated to leave a residue which crystallized when taken up in petrol ether. The colourless prisms m.p. 62-63°

were crystallized twice again yielding 0.22 g. of m.p. 63°-64°. Three further crystallizations did not change the melting point.

Analysis—Found : C, 74.8 ; H, 7.44 ; OMe, 17.6.

$C_{22}H_{26}O_4$ requires : C, 74.55 ; H, 7.39 ; OMe, 17.5.

Methylation of 7-hydroxy-5-methoxy-8-β-phenylpropionyl-2 : 2-dimethylchroman (0.4 g.) by the method described by Backhouse and Robertson (6) yielded a mixture of unchanged material and the dimethoxy compound m.p. 63-64° described above as proved by mixed melting point.

For this compound Backhouse and Robertson (6) reported colourless prisms m.p. 74° from light petroleum.

5′-Methoxy-2 : 2′ : 2′-trimethylchromano-8′ : 7 : 5 : 6-γ-pyrone.

This compound was prepared from dihydro*allo*evodionol substantially as described by Backhouse and Robertson (6), but without attempting to isolate the β-diketone intermediate. The product was isolated as oblique plates, m.p. 168-169° from petrol ether.

Analysis—Found : C, 70.5 ; H, 6.57 (after drying at 110°).

Calculated for $C_{16}H_{18}O_4$: C, 70.01 ; H, 6.61.

The piperonylidene derivative of this γ-pyrone formed yellowish brown needles melting at 223-225° with previous sintering. For these two substances Backhouse and Robertson (6) report m.p. 168° and m.p. 224° respectively.

Methyl-evodionol for Medicosma cunninghamii.

The colourless crystalline solid which separated from the mother liquors of the *allo*evodionol, when purified, crystallized from alcohol as plates, m.p. 78-78.5°. Lahey and Jones (1) record 79° for methyl-evodionol prepared by the methylation of evodionol.

Analysis—Found : C, 68.5 ; H, 6.91 ; OMe, 22.8 ; M..W, 268.

Calculated for $C_{13}H_{12}O_2(OCH_3)_2$: C, 68.66 ; H, 6.91 ; OMe, 23.7 ; M.W., 262.

A sample of methyl-evodionol prepared from a genuine sample of evodionol from *Evodia littoralis* caused no depression of the melting point of the material from *Medicosma cunninghamii.*

The benzylidene derivative was prepared by dissolving 2 g. of the substance m.p. 78-78.5°, 2 ml. of benzaldehyde and 0.5 g. of caustic potash in a minimum quantity of warm alcohol. Yellow needles separated in a few minutes and were filtered after standing overnight. Yield 2.3 g. By crystallization the melting point was raised to 113-113.5° not depressed on admixture of authentic benzylidene-methyl-evodionol.

The 2 : 4-dinitrophenylhydrazone of the substance m.p. 78-78.5° was prepared by the use of Brady's reagent, as stout red needles or prisms m.p. 169.5-170.5° after crystallization from ethyl alcohol. Dr. F. N. Lahey in a private communication states that the previously reported value of 157° (1, 3) for the melting point of this compound is incorrect and should have read 169-170°.

The author wishes to thank Professor T. G. H. Jones for his helpful advice and encouragement, and also Mr. G. Lahey for much aid in the isolation of the materials used in this work, for the preparation of the dinitrophenylhydrazone and the benzylidene derivative of *allo*evodionol and for other assistance.

REFERENCES

1. Lahey and Jones, Queensland University Papers, Chem., **1**, No. 13 (1939).
2. Jones and Wright, Queensland University Papers, Chem., **1**, No. 27 (1946).
3. Lahey, Queensland University Papers, Chem., **1**, No. 17 (1940).
4. Lahey, Queensland University Papers, Chem., **1**, No. 20 (1942).
5. Wright, private communication.
6. Backhouse and Robertson, J.C.S., (1939), 1257.
7. Robertson and Subramanian, J.C.S., (1937), 1545.
8. McGookin, Robertson and Tittensor, J.C.S., (1939), 1587.
9. Fuson and Tullock, J.A.C.S., **56**, 1638 (1934).
10. Clark, " Semimicro Quantitative Organic Analysis," p. 68 (1943).