Phytochemistry, 1975. Vol. 14, pp. 265–269. Pergamon Press. Printed in England.

XANTHONES AND 4-PHENYLCOUMARINS OF *MESUA THWAITESII**

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(*Received* 2 *May* 1974)

Key Word Index—*Mesua thwaitesii*; Guttiferae; xanthones; GC–MS identification of 4-phenylcoumarins.

Abstract—The constituents of the bark, timber and seeds of *Mesua thwaitesii* were examined by column chromatography and GC–MS. 1,5-Dihydroxyxanthone, 1,7-dihydroxyxanthone (euxanthone), 1,3-dimethoxy-5-hydroxyxanthone, 1,5,6-trihydroxyxanthone, mammeisin, (4-phenylcoumarin) and sitosterol have been characterized. Nine 4-phenylcoumarins including mammeigin, mesuagin, mammeisin, mesuol, or its isomers, have been identified in the seed extract. One coumarin has not been previously reported.

INTRODUCTION

Mesua ferrea L. (Guttiferae: subfamily Calophylloideae) is the only species that has been chemically studied from the genus *Mesua*. Investigations have resulted in the isolation and identification of the four 4-phenylcoumarins mesuol (**2**a) [1], mesuagin (**3**a) [3], mammeisin (**2**b) [4], mammeigin (**3**b) [2,3] from the seed oil of *Mesua ferrea* L. The 4-alkylcoumarins ferruol A (**4**a) and mammein (**4**b) have been isolated from the trunk bark of the tree [5] and the heartwood has yielded 1,7-dihydroxyxanthone (**1**b), 1,5-dihydroxy-3-methoxyxanthone (**1**e), 1,5,6-trihydroxyxanthone (**1**d), 1,5-dihydroxyxanthone (**1**a), 1-hydroxy-7-methoxyxanthone (**1**f) and sitosterol [6].

Mesua thwaitesii Planch and Triana (Sinhala-Diya na) is endemic to Ceylon and found generally in the wet zone forests of Ceylon. The tree has good timber properties.

RESULTS AND DISCUSSION

The cold light petrol. extract of the timber gave after chromatography on silica gel sitosterol only. The hot benzene extract of the timber gave a yellow solid and a yellow oil. Column chromatography (silica gel) of the yellow solid gave four pigments, whose UV and IR absorptions were characteristic of xanthones. The two least polar compounds were isomeric and had a molecular ion at *m/e* 228 in its MS. Their physical and spectroscopic data indicated that they were 1,5-dihydroxyxanthone (**1**a, least polar) and 1,7-dihydroxyxanthone (**1**b) and this identification was confirmed by comparison of the xanthones and their dimethyl ethers with authentic samples. The third compound showed in its NMR spectrum the presence of two methoxy groups and five aromatic protons. The absence of any change in the UV maxima on the addition of $AlCl_3$ and the lack of low field signals in the NMR showed the absence of any chelated hydroxy groups in its structure. Comparison of its physical and spectroscopic data with that reported for 1,3-dimethoxy-5-hydroxyxanthone [10] indicated this structure for the compound. Acetylation and methylation yielded the 1,3-dimethoxy-5-acetoxyxanthone (**1**i) and 1,3,5-trimethoxyxanthone (**1**j) respectively, both of which had identical m.p., UV, IR and NMR data to that reported for these compounds [10]. The most polar compound was identified as 1,5,6-trihydroxyxanthone (**1**d) [6] by comparison of the compound and its methyl ether (**1**k) with authentic

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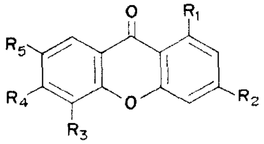
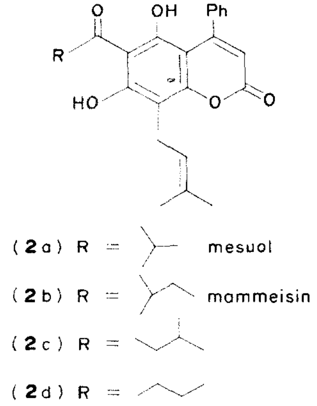
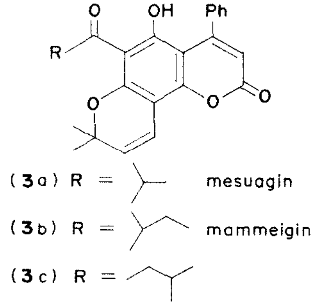
* Part XI in the series "Chemical Investigation of Ceylonese Plants".



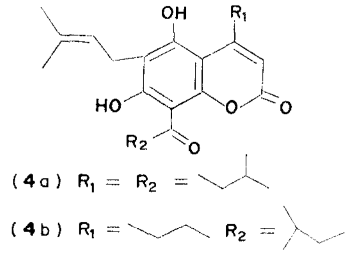
(1a) $R_1 = R_3 = OH$ $R_2 = R_4 = R_5 = H$
(1b) $R_1 = R_5 = OH$ $R_2 = R_3 = R_4 = H$
(1c) $R_3 = OH$ $R_4 = R_5 = H$, $R_1 = R_2 = OMe$
(1d) $R_1 = R_3 = R_4 = OH$ $R_2 = R_5 = H$
(1e) $R_1 = R_3 = OH$ $R_4 = R_5 = H$, $R_2 = OMe$
(1f) $R_1 = OH$ $R_2 = R_3 = R_4 = H$, $R_5 = OMe$
(1g) $R_2 = R_4 = R_5 = H$, $R_1 = R_3 = OMe$
(1h) $R_2 = R_3 = R_4 = H$, $R_1 = R_5 = OMe$
(1i) $R_4 = R_5 = H$, $R_3 = OCOCH_3$, $R_1 = R_2 = OMe$
(1j) $R_4 = R_5 = H$, $R_1 = R_2 = R_3 = OMe$
(1k) $R_2 = R_5 = H$, $R_1 = R_3 = R_4 = OMe$



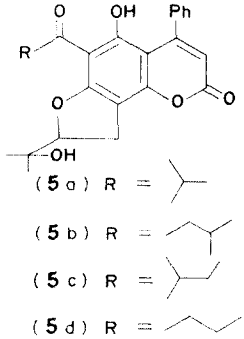
(2a) R = mesuol
(2b) R = mammeisin
(2c) R =
(2d) R =



(3a) R = mesuagin
(3b) R = mammeigin
(3c) R =



(4a) $R_1 = R_2 =$
(4b) $R_1 =$ $R_2 =$



(5a) R =
(5b) R =
(5c) R =
(5d) R =

samples. TLC examination of the hot methanol extract of the timber showed its composition to be very similar to that of the hot benzene extract.

The cold light petroleum extract of the bark was washed successively with aq. Na_2CO_3 and NaOH. The neutral fraction yielded only sitosterol. Acidification of the Na_2CO_3 soluble fraction gave a resinous gum which on repeated preparative TLC gave an unidentified acid of MW 562. Column chromatography (silica gel) of the acidified NaOH soluble fraction gave a yellow solid (λ_{max} 232, 282, 348 nm) which showed the characteristic base shift (λ_{max} 249, 280 sh, 316, 428 nm) of a 6-acylcoumarin [11,14]. Signals at τ 8·69 (3H, *s*) in its NMR are consistent with the presence of a α-hydroxyisopropyl dihydrofuran system while the signals at τ 9·03 (6H, *d*, *J* 7 Hz), 7·80 (1H, *m*), 7·10 (2H, *m*) indicated the presence of a 3-methylbutyryl side chain. Its MS is consistent with 1,2-dihydro-5-hydroxy-2-(1-hydroxy-1-methylethyl)-4-(3-methylbutyryl)-6-phenyl-furo [2,3-h] [1] benzopyran-8-one(**5c**) [12]. Comparison with authentic sample of (**5c**) confirmed the identity.

Extraction of the bark with hot benzene gave a gum which yielded a light petroleum extract which was similar to the cold light petroleum extract obtained previously (TLC examination). The residue of the benzene extract was dissolved in ether and the solution extracted successively with aqueous Na_2CO_3 and NaOH. Chromatography of the Na_2CO_3 and NaOH extracts yielded xanthones (**1a**), (**1c**), (**1d**) and (**1a**), (**1b**) respectively.

Hot extraction of the seeds with light petroleum gave a dark brown oil from which a yellow solid separated out. Repeated separation of the solid on preparative TLC gave three yellow solids. The least polar had MW 406, showed in its NMR spectrum the presence of 3-methylbutyryl side chain, and signals at τ 4·73 (1H, *t*), 6·43 (2H, *d*, *J* 7 Hz), 8·11 (3H, *s*) and 8·24 (3H, *s*) indicated the presence of a 3,3-dimethylallyl substituent. Its mass spectrum had strong ions at *m/e* 406, 349, 351 and 293. This spectral data is consistent with the structure of mammeisin (**2b**) [11] and comparison with authentic material confirmed the identity. The NMR and MS of the most polar constituent showed it to be a mixture of two components, one of which was recognized as the coumarin (**5c**) and the other, probably its lower homologue, (**5a**). In the NMR spectrum in addition to the signals of the coumarin (**5c**) there was a doublet at τ 8·85 (J 7 Hz), a multiplet at τ 6·2 and chelated hydroxyl signal at τ $-4{\cdot}52$ (s). These signals are assigned to an isobutyryl substituent c.f. mesuol (**2a**) [1]. The presence of an ion at *m/e* 408 in its mass spectrum provided additional evidence for the presence of the lower homologue 1,2-dihydro-5-hydroxy-2-(1-hydroxy-1-methylethyl)-4-(2-methylpropionyl)-6-phenyl-furo [2,3-h] [1] benzopyran-8-one (**5a**) which was confirmed by GC–MS examination of the sample.

Preparative TLC of the oil obtained from the light petroleum extract of the seeds yielded three fractions (X, Y and Z) which were subsequently examined by GLC. Fraction Z (low R_f) showed no peaks and was not examined further. The higher R_f fractions (X, Y) showed a number of GC peaks and they were investigated by combined GC–MS. Not all the components were completely resolved but since the mass spectrometer was on line to a computer the GC trace was repetitively scanned and the peaks examined by mass chromatography. Peak A had prominent ions at *m/e* 390, 375, 357 and 347 in its MS and this spectrum in combination with the peak's retention time indicated that it was mesuagin (**3a**) [3,13]. Similarly prominent ions at *m/e* 404, 389, 371, 347 in the MS of peak C together with its retention time enabled its identification as mammeigin (**3b**). Peak B was more complex, one of the MS obtained from this peak had ions at *m/e* 404, 389, 371 and 347 which together with its retention time indicated the presence of the coumarin (**3c**) [13]. The presence of further ions in the spectrum at *m/e* 406, 351, 349 and 293 were indicative of the presence of mammeisin (**2b**) or its isomer (**2c**) or both in the peak [14]. Examination of a subsequent mass spectrum obtained from peak B showed the presence of an additional ion at *m/e* 392, indicative of the presence of mesuol (**2a**) or its isomer (**2d**) and on the basis of its retention time the latter structure is preferred.

In order to obtain further information about the nature of peak B relevant mass chromatograms were examined. Spectra numbers 614–621 were taken during the elution of peak B; the molecular ion (*m/e* 392) of both (**2a**) and (**2d**) indicated the presence of the ion in spectrum number 619. Examination of the mass chromatograms of the molecular ion (*m/e* 406) and major fragment ion (*m/e* 349) of mammeisin (**2b**) and its isomer (**2c**) shows the presence of maxima for these ions in spectra numbers 618 and 621 and they were assigned to (**2c**) and (**2b**) respectively on the basis of their retention times. Confirmation of the structural assignments made for the components of fraction X was provided by comparison with authentic sample (MS and GC retention time). The total ion current trace of sample Y also showed three peaks. However, all proved to be due to single components. Examination of the MS of peak A (*m/e* % rel. int.) 408 (45), 365 (78), 347 (38), 307 (38), 293 (100) and comparison of it with the mass spectra of the coumarins (**5b**) and (**5c**) [15] indicated that it had structure (**5a**) or the isomeric structure (**5d**), since the only major difference in its spectrum was the presence of a molecular ion at *m/e* 408. On the basis of retention time data, structure (**5a**) is preferred for this compound and it is the first report of its presence. in plant extracts. Components B and C had major ions at *m/e* (% rel. int.) 422 (44), 365 (98), 347 (26), 307 (29), 293 (100) and 422 (28), 365 (100), 347 (15), 307 (19), 293 (68) respectively, and these spectra are similar to those reported for the coumarins (**5b**) and (**5c**) isolated from *Mammea americana* [15]. That these were indeed correct structural assignments was comfirmed by comparison with authentic samples (MS and GC retention time).

Our studies have confirmed the presence of the 4-phenylcoumarins and the xanthones (**1a**), (**1b**) and sitosterol previously reported from *Mesua ferrea* and also resulted in the characterization of the xanthone (**1c**) and the 4-phenylcoumarins **5**(a–c), **2c** and **3c**. The 4-phenylcoumarin (**5a**) has not previously been reported. Our studies revealed that no 4-alkylcoumarins were present in *M. thwaitesii.*

EXPERIMENTAL

Chemical shifts are recorded in τ values. Rotations were determined with a Bellingham and Stanley polarimeter. Microanalytical results were obtained from CSIRO. Microanalytical Service, Melbourne, Australia. Separation by column chromatography was carried out with Merck silica gel mesh 30–70. TLC was with Merck silica gel. M.ps were determined on Kofler Hot Stage and are uncorrected. The alkali washings of the extracts were carried out at 5°. Yields of extracts are expressed as percentage of the dry wt of plant material used. GC–MS data were obtained using Varian 1700 GC coupled to a Varian CH 5D MS by an all-glass inlet system incorporating a two-stage Watson–Biemann separator. MS (ionizing potential 70 eV, source temp. 220°) were obtained in line diagram and mass list form with background substracted and corrected for change in total ionization during each scan with the aid of a

Varian 620i computer on line to the mass spectrometer, using Kosmic 2 programmes. These programmes were also used to obtain plots of mass against time and to reconstruct total ionization traces of the GC.

Plant material. The timber and the bark were separated, chipped and powdered in a mill and extractives obtained successively with light petroleum (60–80°) C_6H_6 and MeOH. The solvents were removed under red. press. and the fractions worked up as detailed below. The pericarp and the seeds of the fruit were separated, powdered and extracted with light petrol. in Soxhlet type apparatus.

Extractives from the timber: cold light petroleum extract: sitosterol. Cold extraction of the timber (10 kg) with light petrol. (60–80°) (10 l.) for 7 days gave on concn and filtration a crude white solid which on repeated crystallization from ethanol afforded sitosterol (0·012 mg) m.p. 136° (lit. [16] 136–7°); $[\alpha]_D^{28}$ $-35{\cdot}1°$ ($CHCl_3$) (lit. [16]). $[\alpha]_D$ $-36°$.

Hot C_6H_6 extract. Hot C_6H_6 extraction of the timber with C_6H_6 (10 l.) for 7 days in a Soxhlet deposited a yellow solid (14 g) which was filtered and the filtrate on removal of solvent gave a gum (21 g, 0·2%).

1,5-*Dihydroxyanthone* (**1**a). The yellow solid (4 g) was chromatographed on silica gel (200 g). Elution with C_6H_6 gave a pale yellow solid (0·520 g) which on purification by preparative TLC ($CHCl_3$–HOAc, 92:8) and recrystallization from C_6H_{10} gave 1,5-dihydroxyxanthone (0·15 g) as pale yellow needles m.p. 268–70° (lit. [18] 268–70°). It was identical with an authentic sample (mixed m.p., IR and TLC). It gave a dimethyl ether (**1**g) m.p. 194° (lit. [19] 194–196°). 1,5-Dihydroxyxanthone (0·05 g) in methanol (30 ml) was treated with excess ethereal diazomethane and the usual work-up gave 1-hydroxy-5-methoxyxanthone (0·035 g) m.p. 213° (lit. [17] 214–15°).

1,7-*Dihydroxyxanthone* (*Euxanthone*) (**1**b). Further elution of the column with C_6H_6–$CHCl_3$ (1:2) gave a yellow solid which on crystallization from toluene yielded euxanthone (0·300 g) as bright yellow needles m.p. 238–39° (lit. [21] 238–40°). It was identical with an authentic sample (m.m.p., IR and TLC). It gave a dimethyl ether (**1**h) as needles m.p. 150–51° (lit. [6] 150–52°). It was identical with an authentic sample (mixed m.p., and TLC). Euxanthone (0·050 g) in methanol (30 ml) was treated with excess ethereal CH_2N_2 for 4 hr and the usual work-up followed by recrystallization from EtOH gave 1-hydroxy-7-methoxyxanthone (**1**f) (0·025 g) as pale yellow needles m.p. 127–28° (lit. [7] 128–29°).

1,3-*Dimethoxy*-5-*hydroxyxanthone* (**1**c). Further elution of the column with $CHCl_3$ gave a pale yellow solid (1·7 g) which on TLC was found to be a mixture of 1,3-dimethoxy-5-hydroxyxanthone and 1,5,6-trihydroxyxanthone. This solid (1 g) was chromatographed on acid washed silica gel (50 g) column. Elution with $CHCl_3$ and recrystallization from ethanol gave 1,3-dimethoxy-5-hydroxyxanthone (0·080 g) as yellow cubes m.p. 262–64° (lit. [18] 263–65°); λ_{max} (EtOH) 248 (log ϵ 4·62), 305 (4·25) and 344 (3·66) nm. No alteration in the presence of $AlCl_3$. ν_{max} (KBr) 1520, 1580, 1640 and 3200 cm^{-1}. τ (trifluoroacetic acid 100 MHz) 2·00 (1H, *q*, *J* 6·5, 3·5 Hz, 8-H); 2·20–2·60 (2H, *m*, 6, 7-H); 2·92 (1H, *d*, *J* 2·5 Hz, 4-H); 3·18 (1H, *d*, *J* 2·5 Hz, 2-H); 5·65 (3H, *s*, 1-OMe); 5·84 (3H, *s*, 3-OMe). Found C, 66·20; H, 4·48%. Calc. for $C_{15}H_{12}O_5$ C, 66·17; H, 4·44%. The acetate (**1**i) had m.p. 178–79° (lit. [10] 179–80°); λ_{max}^{EtOH} 238 (log ϵ 4·46), 297 (4·11) and 331 (3·69) nm τ ($CDCl_3$, 100 MHz) 1·83 (1H, *q*, *J* 6·5, 3·5 Hz, 8-H); 2·65–2·87 (2H, *m*, 6, 7-H); 3·58 (1H, *d*, *J* 2·5 Hz, 4-H); 3·68 (1H, *d*, *J* 2·5 Hz, 2-H); 6·02 (3H, *s*, 1-OMe); 6·16 (3H, *s*, 3-OMe); 7·59 (3H, *s*, 5-OAc). The methyl ether (**1**j) had m.p. 222–223° (lit. [10] 222–225°).

1,5,6-*Trihydroxyxanthone* (**1**d). Further elution of the above column with $CHCl_3$–MeOH (9:1) gave a pale yellow solid which on purification by preparative TLC ($CHCl_3$–HOAc, 5:1) and recrystallization from acetone afforded 1,5,6-trihydroxyxanthone (0·05 g), as pale yellow needles, m.p. 286–287° (lit. [6] 288–290°). It was identical with an authentic sample (m.m.p., IR and CO TLC). The trimethyl ether (**1**k) (0·025 g) needles m.p. 151° (lit. [6] 150–151°) was identical with an authentic sample (m.m.p. and CO TLC).

Extractives of the bark: Light petroleum extract. Cold extraction of the bark (8·6 kg) with light petrol. (60–80°) (10 l.) for 7 days gave a gum (130 g, 1·5%) on removal of the solvent. This gum (20 g) was dissolved in Et_2O (1·5 l.) and washed with ice cold 10% aq. Na_2CO_3 and (10%) aq. NaOH. The Et_2O layer was concnd to give a gum (6 g). This gum (2 g) on being chromatographed on neutral alumina (70 g) gave sitosterol (0·200 g). Acidification of the sodium carbonate washings and the usual work-up gave a material (11·28 g). This material (2 g) on preparative TLC yielded an unidentified acid (0·120 g), m.p. 69–70° $[\alpha]_D^{28}$ + 45° ($CHCl_3$) M^+ 562·32914.

1,2-*Dihydro*-5-*hydroxy*-2-(1-*hydroxy*-1-*methylethyl*)-4-(3-*methylbutyryl*)-6-*phenyl*-*furo* [2,3-*h*] [1] *benzopyran*-8-*one* (**5**c). Acidification of the NaOH washings and the usual work-up gave a gum (3·28 g). This material was chromatographed over acid washed silica gel. Elution with $CHCl_3$ and recrystallization from Me_2CO gave coumarin (**5**c) as yellow cubes (0·100 g). λ_{max} (EtOH) 232 (log ϵ 4·11), 282 (4·30) and 348 (4·04) nm. λ_{max} (EtOH–KOH) 249 (log ϵ 4·22), 280 sh (4·04), 316 (4·01) and 428 (3·95) nm. ν_{max} (KBr) 1713, 3240 and 3420 cm^{-1}. *m/e* 422, 365, 347, 303, 293. τ ($CDCl_3$, 60 MHz) $-4{\cdot}45$ (1H, *s*, 5-OH); 2·64 (5H, *m*, 4-Ph); 4·09 (1H, *s*, 3-H); 5·09 (1H, *t*, *J* 9 Hz, 5′-H); 6·69 (2H, *d*, *J* 9 Hz, 4′-H); 7·10 (2H, *m*, 2-butyryl H); 8·32 (1H, Br, 5′-(1-hydroxy); 8·57 and 8·69 (6H, 2*s*, 5′-gemdimethyl); 9·03 (6H, *d*, *J* 7 Hz, $C(Me)_2$). It was identical with an authentic sample (IR and CO TLC).

Hot C_6H_6 extracts. Hot C_6H_6 extraction with C_6H_6 (10 l.) for 7 days in a Soxhlet gave a gum (30 g, 0·34%). This gum (5 g) was dissolved in Et_2O (1·5 l.) and washed successively with ice cold aq. soln of 10% aq. Na_2CO_3 and 10% aq. NaOH. Et_2O layer on concn gave a gum which was not further investigated. Acidification of the Na_2CO_3 washings with 15% HCl gave a yellow solid (1·9 g). This solid (1·5 g) on being chromatographed on acid washed silica gel (50 g), elution with C_6H_6–$CHCl_3$ (3:1) yielded 1,5-dihydroxyxanthone (0·185 g). Further elution of the column with C_6H_6–$CHCl_3$ (1:3) gave 1,3-dimethoxy-5-hydroxyxanthone (**1**c) (0·140 g). Elution with $CHCl_3$–MeOH (100:1) gave 1,5,6-trihydroxyxanthone (**1**d) (0·020 g). Acidification of the NaOH washings gave a yellow solid (1·1 g). This solid (1 g) was chromatographed in acid washed silica gel. Elution with C_6H_6–$CHCl_3$ (3:1) gave 1,5-dihydroxyxanthone. Elution with C_6H_6–$CHCl_3$ (1:1) afforded euxanthone (0·320 g).

Extractives of the seeds—isolation of mammeisin. Hot extraction of the seeds (200 g) with light petrol. (60–80°) for 2 days gave a dark brown oil (15 g) (7·5%) from which separated out a yellow solid (1·2 g, 0·6%). Three components were obtained by separation of this solid (0·800 g) by preparative TLC. First component on crystallization from acetone afforded pale yellow cubes of mammeisin [4] (0·120 g) m.p. 102° (lit. [4] 98–102°) *m/e* 406, 349. It was identical with an authentic sample (m.m.p., IR and CO–TLC).

Acknowledgements—The authors thank Professors W. D. Ollis, University of Sheffield, R. H. Thomson, University of Aberdeen, and Dr. P. Bladon, University of Strathclyde, for providing most of the spectral data; Professor L. Crombie, University of Nottingham, Professor K. Venkataraman, National Chemical Laboratories, Poona, India, and Dr. F. Scheinmann, University of Salford, for authentic samples; and Dr. S. Balasubramaniam, Department of Botany, Peradeniya Campus, for identification of the plant. They also thank the National Science Council of

Sri Lanka for a grant and the Science Research Council (U.K.) for financial assistance in the purchase of the Varian CH5D mass spectrometer and Professor A. H. Jackson, of the University College, Cardiff, for advice and encouragement.

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