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CHEMICAL CONSTITUENTS OF THE HEARTWOOD OF *MESUA FERREA*

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Abstract—The heartwood of *Mesua ferrea* L. was found to contain 1,5-dihydroxyxanthone (II), euxanthone 7-methyl ether (IV) and β-sitosterol, in addition to the two xanthones previously isolated. Salient features of the i.r. and NMR spectra of xanthones are discussed.

INTRODUCTION

Since we have initiated an investigation on the chemical constituents of the heartwood of *Mesua ferrea* L. (Guttiferae), two relevant reports have appeared.[1] This tree is commonly called ironwood in Malaya and is indigenous to Asia. The hard and durable trunk-wood is used widely in agricultural tools and vehicles in the south-east Asian countries. From our work we isolated and identified three more compounds in addition to previously reported constituents.[1]

RESULTS AND DISCUSSION

The acetone extract of the heartwood was first separated into methylene chloride soluble and insoluble parts and the constituents of the soluble fraction were studied. Partial evaporation of the solvent afforded a deposit of a yellow solid; the rest of the semi-solid was taken up into ethyl acetate and separated into "strong", "medium" and "weak" acid fractions and into a "neutral" fraction (see Experimental). It was clear that the tree contained very little neutral compounds ($<0{\cdot}1$ per cent of wood), but mostly phenolics as usually encountered in the Guttiferae family.[2–4] From the neutral fraction, β-sitosterol, the steroid widely distributed in the plant kingdom, was isolated and identified.

The isolation of the phenolic compounds was carried out by standard alumina column chromatography and also by preparative thin-layer chromatography (TLC) in one case. These operations resulted in isolation of four well-defined xanthones as indicated by their i.r. and u.v. spectra. Among them 1,5-dihydroxy-3-methoxyxanthone (I) and euxanthone (III) have been isolated by the Indian authors.[1] Interestingly euxanthone-7-methyl ether (IV) was isolated in the neutral fraction probably due to the weak acidity of the *peri* phenolic group at C-1. The isolation of IV from *Kielmeyera corymbosa* of Brazilian origin has been claimed, but the details of the characterization are not available.[5] Its isolation from a *Mesua*

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[1] T. R. Govindachari, B. R. Pai, P. S. Subramaniam, U. Ramdes Rao and N. Muthukumaraswamy, *Tetrahedron* 23, 243, 4161 (1967).

[2] O. R. Gottlieb, *Phytochem.* 7, 411 (1968).

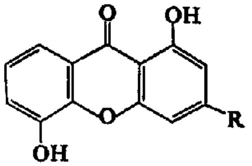
[3] F. M. Dean, *Naturally Occurring Oxygen Ring Compounds*, p. 266, Butterworths, London (1965).

[4] The references are far too extensive to be listed here. An up-to-date listing of references are available in Ref. 2.

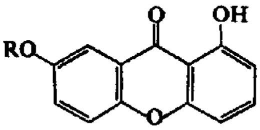
[5] L. D. Antonaccio, L. G. Fonseca e Silva, D. de Barros Correa, O. R. Gottlieb and M. R. Magalthaes, *Anais Acad. Brasil. Cienc.* 37, (2), 229 (1965).

species however has never been demonstrated. Since the m.p. of our IV (and the acetate of IV) agrees with the reported 7-methyl ether (and the corresponding acetate) as synthesized by methylation of euxanthone,[6] the identity of the compound is established. The correctness of the structure is indicated by the method of preparation and proven by the presence of the NMR signal of the phenolic hydroxyl proton at C-1 (see Experimental) at a low field (τ $-2{\cdot}41$) and the methoxy proton at τ 6·20. The shift to a low field of the phenolic proton at C-1 is, no doubt, due to the intramolecular hydrogen bonding similar to the case of acetylacetone[7] and the typical range for the xanthone series[8–10] appears to be between τ $-2{\cdot}4$–$-2{\cdot}8$. In agreement with their intramolecular hydrogen-bonded enol ketone structures, all these xanthones show diffused OH stretching absorptions in the i.r. at 2700–3100 cm^{-1} reminiscent of carboxylic acid OH absorption. These characteristics disappear on acetylation.

The xanthone of m.p. 259–261° was eventually shown to be 1,5-dihydroxyxanthone (II), the only unknown dihydroxyanthone at the time of isolation. While our work was in progress, a preliminary communication[11] on the isolation of this xanthone (m.p. 260°–261°) from *Mammea americana* L. and a brief description of the synthesis (m.p. 265–266°) were announced. In the following we present independent evidence leading to this structure.



(I) R = OCH_3
(II) R = H



(III) R = H
(IV) R = CH_3

The diacetate of II showed M^+ peak at 312 and the NMR signals for the two non-equivalent acetoxy methyls at τ 7·55 and 7·59. The i.r. spectrum of the diacetate showed the expected absorption pattern in comparison to II (see Experimental). The parent xanthone (II) therefore must be $C_{13}H_8O_4$ and carry two hydroxyl groups attaching to the nucleus. One of the hydroxyl groups must be placed at C-1 since II shows one proton signal at τ $-2{\cdot}40$ which is D_2O exchangeable. A survey of the published NMR data on xanthones[8–10, 12] clearly indicates that the C-8 aromatic proton tends to resonate at somewhat lower fields (τ 2·1–1·9 in $CDCl_3$ solution), due to an anisotropic effect of the carbonyl group,[13] and shifts (from this range) to slightly higher field (by 0·2–0·4 ppm) if the C-7 position is oxygenated. The overall NMR pattern of the diacetate of II exhibits a superimposed pattern of two similar ABC systems in which one proton double doublets ($J = 8$ and 2·5 cps) at τ 1·92 are clearly

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[6] K. S. Pankajamani and T. R. Seshadri, *J. Sci. Ind. Res. (India)*, **13B**, 396 (1954).

[7] L. M. Jackman, *Application of NMR Spectroscopy in Organic Chemistry*, p. 70, Pergamon Press, London (1959).

[8] E. D. Burling, A. Hefferson and F. Scheinmann, *Tetrahedron* **21**, 2653 (1965).

[9] O. R. Gottlieb, M. Toveira Magalhães, M. Camey, A. A. Lins Mesquita and D. de Barros Carrêa, *Tetrahedron* **22**, 1777 (1966).

[10] H. D. Locksley, I. Moore and F. Scheinmann, *J. Chem. Soc.* (c) 430 (1966).

[11] R. A. Finnegan, J. K. Patel and P. L. Backman, *Tetrahedron Letters* 6087 (1966).

[12] The survey of the NMR data was based on that in the recent publications as quoted in Ref. 2.

[13] P. 124 of Ref. 7.

discernible.[14] This feature demands that the second hydroxyl group cannot be placed at C-8 nor at C-2, C-3 and C-4. It also indicates the C-6 and C-7 are unlikely positions to place the hydroxyl group because of the coupling pattern at C-8 (*ortho* and *meta* coupling). This is further confirmed by comparison of the melting points and u.v. data of II (and the corresponding acetate) with those of euxanthone and 1,6-dihydroxyxanthone (and the corresponding acetates).[15] Indeed a comparison of u.v. data of II with that of other dihydroxyxanthones established the similarity with the reported maxima of 1,5-dihydroxyxanthone, but not of others.[15] Therefore II must be 1,5-dihydroxyxanthone.

In a current biogenetic theory,[2] II is one of the parent members of xanthones that can be derived from shikimides and polyketides scheme. Isolation of this compound provides a link in the scheme.

EXPERIMENTAL

Melting points were taken with a Fisher-Johns hot stage and were uncorrected. Unless specified otherwise, the u.v. spectra were recorded in ethanol with a Cary 14 recording spectrophotometer, the i.r. spectra in nujol mulls with a Perkin Elmer 457 grating spectrometer and NMR spectra with a Varian Associates A56/60 spectrometer. The mass spectra were taken with a Hitachi-Perkin Elmer RMU-6E spectrometer with direct insertion of samples. Analytical and preparative TLC plates were prepared with silica G supplied by Stahl. The NMR data were described with the following abbreviations: singlet (S), triplet (T), double doublets (DD), multiplet (M) and the number of protons (H).

Extraction and Fractionation

A sample of the heartwood of *Mesua ferrea L.* was obtained from McRitchi Reservoir through the courtesy of the Botanical Gardens, Singapore. The ground heartwood (3 kg) was extracted with acetone in a Soxhlet for 10 hr. Removal of solvent left a dark reddish residue (300 g). This residue (250 g) was stirred with CH_2Cl_2 (1 l.) and the solution was separated. On evaporation of CH_2Cl_2 to *ca.* 200 ml, a yellow solid (6·5 g, A) deposited after cooling. The CH_2Cl_2 solution after removal of the solid A was evaporated to dryness to give an amorphous solid (35·8 g). This solid was taken up in EtOAc (200 ml) and successively shaken with saturated aqu. $NaHCO_3$, 10% Na_2CO_3 solution and then 1 N NaOH leaving a "neutral" fraction (2·5 g, B) after removal of the solvent.

The fraction extracted with 10% Na_2CO_3 was liberated with 1 N HCl and was worked up in the usual manner to give an amorphous solid (11·2 g, C). In a similar manner, the fraction extracted with 1 N NaOH gave a solid (11·6 g, D).

Isolation of the Constituents

Fraction A. A part of Fraction A (1·50 g) was taken up in EtOAc and was absorbed on an alumina column. Elution with 1:1 mixture of benzene–ether gave a yellow solid which was recrystallized to give 1,5-dihydroxy-3-methoxy-xanthone (I, 124 mg), m.p. 271–272°, M^+ 258, λ_{max} (log ϵ) 248 (4·44), 273 (shoulder, 3·88), 310 (4·01) and 354 (3·59) nm and the i.r. peaks at 3450, 1664, 1590, 1510, 1280 and 1150 cm^{-1}. I showed the NMR signals (DMSO) at τ −2·80, −0·25 (both D_2O exchangeable), 2·52 (DD, $J=6$ and 3·5 cps), 2·61–2·88 (M, 2H) and an AB quartet at at τ 3·46 and 3·70 ($J=2·5$ cps). The u.v. maxima and m.p. are in good agreement with reported values (lit. m.p. is 270–272°)! The acetate was recrystallized from benzene–petrol. ether to give plates, m.p. 159–161° (lit.[1] 158–160°), the NMR signals ($CDCl_3$) at τ 2·00 (DD, $J=8$ and 3 cps), 6·17 (S, 3H), 7·58 (S, 3H) and 7·61 (S, 3H) and an AB quartet at τ 3·34 and 3·51 ($J=2$ cps).

Continuous elution with a 3:7 mixture of benzene–ether yielded 1,5-dihydroxyxanthone (II) (110 mg) which was recrystallized from EtOH–acetone to give yellow needles, m.p. 259–261°, λ_{max} (log ϵ) 233 (4·41), 248 (4·61), 312 (3·89) and 370 (3·66) nm and i.r. peaks at 3320, 1640 and 1580 cm^{-1}. II showed the NMR signals (DMSO) at τ −2·40, −0·24 (both D_2O exchangeable) and 2·19–3·49 (M, 6H). The acetate was recrystallized from ethanol to give a colorless needle, m.p. 214–216°, M^+ 312, λ_{max} (log ϵ) 231 (4·05), 238 (4·10), 262 (3·46) and 338 (3·27) nm and the i.r. ($CHCl_3$) peaks at 1770, 1665, 1625, 1615 and 1182 cm^{-1}. The acetate showed signals ($CDCl_3$) at τ 1·92 (DD, $J=8$ and 2 cps), 3·05 (DD, $J=7·5$ and 1·5 cps), 7·55 (S, 3H) and 7·59 (S, 3H).

Fraction C. This fraction (340 mg) was separated on a preparative TLC plate (0·4 mm silica gel) using 4 per cent acetone in CH_2Cl_2 as eluent. The foremost fraction was isolated in the usual manner to give euxanthone (132 mg) which was recrystallized from EtOH to give yellow needles, m.p. 238–239° (lit.[1] 238–240°),

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[14] J. R. Dyer, *Application of Absorption Spectroscopy of Organic Compounds*, p. 106, Prentice-Hall, Englewood Cliffs, N.J. (1965).

[15] P. Yates, *Structure Determination*, p. 43, Benjamin, New York (1967).

M^+ 228, λ_{max} (log ϵ) 234 (4·45), 258 (4·55), 285 (3·81) and 383 (3·88) nm and the i.r. absorptions at 3318, 1640, 1605 and 1580 cm^{-1}. Euxanthone showed the NMR signals (DMSO) at τ −2·60 and 0·15 (D_2O exchangeable) and 2·13–3·45 (M, 6H). The diacetate was recrystallized from benzene as colorless needles, m.p. 183–185° (lit.[1] 183–184°), the NMR signals ($CDCl_3$) at τ 2·10–3·16 (M, 6H), 7·58 (S, 3H) and 7·74 (S, 3H).

Fraction D. The TLC analysis of this fraction showed the main constituents to be I and II.

Fraction B. This fraction (2·5 g) was dissolved in benzene (3 ml) and was chromatographed on an alumina column. Elution with a mixture of benzene–ether (4:1 ratio) gave β-sitosterol (62 mg) which was recrystallized from methanol, m.p. 137–138°, the acetate recrystallized from methanol, m.p. 125–126°. The mixed m.p. with an authentic sample of β-sitosterol (m.p. 137–138°) gave no depression. β-Sitosterol shows the NMR signals at τ 4·75 (T, 1H) for the olefinic proton, 6·60 (M, 1H) for the 3-*axial* proton and the i.r. peaks at 3500 and 1050 cm^{-1}.

Elution with a mixture of benzene–ether (2:3) gave euxanthone-7-methyl ether (152 mg, IV) which was recrystallized from acetone to give yellow needles, m.p. 128–129° (lit.[6] 126–128°), M^+ 242, λ_{max} (log ϵ) 234 (4·31), 260 (4·40), 286 (3·63) and 380 (3·68) nm and i.r. absorption at 3100, 2700, 1645, 1605 and 1585 cm^{-1}. IV showed the NMR signals ($CDCl_3$) at τ −2·41 (D_2O exchangeable), 2·39–3·50 (M, 6H) and 6·20 (S, 3H). The acetate was recrystallized from EtOH to colorless needles, m.p. 191–193° (lit.[6] 188–190°), λ_{max} (log ϵ) 237 (4·21), 250 (4·17) and 358 (3·65) nm and the i.r. peaks ($CHCl_3$) at 1770, 1650, 1625, 1300 and 1045 cm^{-1}. The acetate showed the NMR signals ($CDCl_3$) at τ 2·51 (DD, $J=3$ and 1 cps), 3·17 (DD, $J=7$ and 1·5), 2·59–2·91 (M, 4H), 6·20 (S, 3H) and 7·57 (S, 3H).