

organic phase was no longer fluorescent. The combined CHCl_3 extract was concd and chromatographed on a Si gel column Na_2CO_3 soln acidified and re-extracted with CHCl_3 . The CHCl_3 extract was concd and chromatographed on a Si gel column (2.5×40 cm), eluting with CHCl_3 .

Isolation and characterization. The early eluates gave crude crystals (250 mg), which were recrystallized from EtOH to yield 1, as colourless needles, mp 129° ; $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 222, 282, (log ϵ 4.408, 4.255); ν_{max} cm^{-1} : 3100, 3010, 2980, 2950, 2850, 1690, 1622, 1583, 1500, 833; PMR (CDCl_3) δ m: 3.88 (3s, 9H, $3 \times \text{OMe}$), 6.36 (d, 1H, $J = 16$ Hz), 6.76 (s, 2H), 7.74 (d, 1H, $J = 16$ Hz), 9.5 (br, 1H, CO_2H); MS m/e : 238 M^+ , 223, 195, 163; FS nm: 424; (Found C, 60.68; H, 6.07. $\text{C}_{12}\text{H}_{14}\text{O}_5$ requires C, 60.51; H, 5.88%). It was identical with 3,4,5-trimethoxycinnamic acid, which was derived from methylation of sinapic acid (TLC, IR, mmp). The later eluates afforded crude crystals (350 mg), which were recrystallized from EtOH to give 2 as colourless needles, mp 225° ; $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 244, 274, 313, 343 sh (log ϵ 4.62, 4.13, 4.35, 4.10), $\lambda_{\text{max}}^{\text{EtOH} + \text{NaOAc}}$ nm: 240, 272 sh, 320 sh, 360 (log ϵ 4.66, 4.11, 4.07, 4.29); ν_{max} cm^{-1} : 3120, 3010, 2950, 2850, 1640, 1617, 1595, 1475, 1460, 1425, 1415, 1280, 1215, 1205, 1125; PMR (CDCl_3) δ_{ppm} : 3.7 (s, 3H, OMe), 3.8–3.83 (3s, 9H, $3 \times \text{OMe}$), 6.45 (1H, OH), 6.67 (s, 1H, C-4H), 6.87 (s, 1H, C-5H), 7.62 (s, 1H, C-8H); PMR (C_6D_6) δ_{ppm} : 3.07, 3.14, 3.73, 4.1 (each s and 3H, $4 \times \text{OMe}$); MS m/e : 332 M^+ , 317, 302, 289, 274, 259, 167; FS nm: 454; (Found C, 61.27; H, 4.78. $\text{C}_{17}\text{H}_{16}\text{O}_7$ requires C, 61.45; H, 4.85%). The solid which was insol. in $\text{Ba}(\text{OH})_2$ soln was extracted several times with MeOH, until the MeOH extract showed no fluorescence. The combined MeOH extracts were evapd *in vacuo* to give a resinous mass (240 g), which was suspended in 10% Na_2CO_3 soln (12 l) and extracted with Et_2O . The Et_2O soln was concd and chromatographed on a Al_2O_3 column (2.5×40 cm) eluting with Et_2O . The early eluates gave crude crystals (2.1 g), which were recrystallized from EtOH to yield 3, as colourless needles, mp 133° ; $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 242, 256, 280, 310, 355 (log ϵ 4.51, 4.51, 4.45, 4.49, 3.78); ν_{max} cm^{-1} : 3040, 2980, 2950, 2850, 1652, 1615, 1595, 1480, 1470, 1460, 1422, 1360, 1285, 1145, 1030, 815; PMR (CH_2Cl_2) δ_{ppm} : 3.81–3.92 (4s, 12H, $4 \times \text{OMe}$), 6.65 (s, 1H, C-4H), 7.2 (dd, 1H, $J = 1.5, 4.8$ Hz, C-6H), 7.3 (dd, $J = 0.5, 4.8$ Hz, C-5H), 7.6 (dd, 1H, $J = 0.5, 1.5$ Hz, C-8H); MS m/e : 316 M^+ , 301, 273, 258, 151; FS nm: 484; (Found C, 64.52; H, 4.98. $\text{C}_{17}\text{H}_{16}\text{O}_6$ requires C, 64.55; H, 5.10%). It was identical with an authentic sample of

1,2,3,7-tetramethoxyxanthone (TLC, IR, and mmp). The later eluates gave crude crystals, which were recrystallized from EtOH to yield 4, mp 183° ; $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 247, 270 sh, 312, 342 sh (log ϵ 4.43, 3.96, 4.15, 3.86), $\lambda_{\text{max}}^{\text{EtOH} + \text{NaOAc}}$ nm: 248, 272, 312, 343 sh (log ϵ 4.42, 3.95, 4.12, 3.83); ν_{max} cm^{-1} : 3010, 2970, 2950, 2850, 1642, 1620, 1610, 1595, 1510, 1475, 1425, 1280, 1270, 1220, 1130, 1060; PMR (CD_2Cl_2) δ_{ppm} : 3.81–3.85 (5 s, 15H, $5 \times \text{OMe}$), 6.68 (s, 1H, C-4H), 6.8 (s, 1H, C-5H), 7.58 (s, 1H, C-8H); PMR (C_6D_6) δ_{ppm} : 3.33, 3.37, 3.48, 3.79, 4.09 (each s and 3H, $5 \times \text{OMe}$); MS m/e : 346 M^+ , 331, 315, 303, 288, 273, 181; FS nm: 468; (Found: C, 62.47; H, 5.27. $\text{C}_{18}\text{H}_{18}\text{O}_7$ requires C, 62.42; H, 5.44%). It was identical with the Me ether of 2, which was derived from the treatment of 2 with $\text{CH}_2\text{N}_2\text{-MeOH}$.

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XANTHONES FROM *LAWSONIA INERMIS*

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Key Word Index—*Lawsonia inermis* (syn. *L. alba*); Lythraceae; lawsone (2-hydroxy-1, 4-naphthaquinone); laxanthone-I (1, 3-dihydroxy-6, 7-dimethoxyxanthone); laxanthone-II (1-hydroxy-3, 6-diacetoxy-7-methoxyxanthone).

Abstract—Two new xanthones isolated from *Lawsonia inermis* have been characterised as 1, 3-dihydroxy-6, 7-dimethoxyxanthone and 1-hydroxy-3, 6-diacetoxy-7-methoxyxanthone and named laxanthone-I and II, respectively.

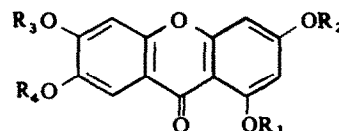
This communication describes the isolation and structural elucidation of two new xanthones from *Lawsonia*

inermis (Syn. *L. alba*) commonly known as henna. Uses of this plant are described in ref. [1] and previous work

in refs [2-8]. The whole plant (2 kg) was extracted exhaustively with hot EtOH and the solvent-free extract chromatographed over Sigel. The petrol eluate gave lawsone, mp 190° [8]. The C₆H₆ eluate on rechromatography over Si gel followed by elution with petrol-C₆H₆ (1:3) gave two compounds laxanthone-I and II.

Laxanthone-I (1). Brownish-green ferric reaction and spectral data showed a chelated OH. Methylation of 1 with CH₂N₂ gave a Me ether (1a) identical with synthetic 1-hydroxy-3, 6, 7-trimethoxyxanthone [9] indicating it to be a 1, 3, 6, 7-tetraoxygenated xanthone. Acetylation of 1 with Ac₂O-Py gave an acetate (1b) which was shown by PMR to contain two methoxys and two acetoxyis. The signals at δ 6.76 and 6.8 assigned to C-2 and C-4 *meta*-coupled protons, had values lower than those noted in the case of 1a. These shifts were therefore attributed to the presence of the two acetoxyis at the C-1 and C-3 positions. Furthermore, laxanthone-I and its acetate were identical with synthetic 1, 3-dihydroxy-6, 7-dimethoxyxanthone and its diacetate [9]. 1, C₁₅H₁₂O₆; mp 286-7°; $\nu_{\text{max}}^{\text{KBr}}$ 3400 (OH), 1750, 1650, (conj. CO) cm⁻¹; $\lambda_{\text{max}}^{\text{MeOH}}$ 240, 310, 360 nm; + AlCl₃ 230, 265, 335, 380 nm. MS. 288 (M⁺), 273, 260, 245, 217 and 203. 1a, C₁₆H₁₄O₆; mp 218-9°; PMR (δ ; CDCl₃): 3.87-3.95 (9H, s, 3X-OMe), 6.27 (1H, *d*, *J* = 2Hz, C-2-H), 6.37 (1H, *d*, *J* = 2Hz, C-4-H), 7.08 (1H, s, C-5-H), 7.57 (1H, s, C-8-H), 13.03 (1H, OH). 1b, C₁₉H₁₆O₈; mp 208-9°; PMR (δ ; CDCl₃): 2.3 (3H, s, C-3-OAc), 2.47 (3H, s, C-1-OAc), 3.95-4 (6H, s, 2x-OMe), 6.76 (1H, *d*, *J* = 2Hz, C-2-H), 6.8 (1H, *d*, *J* = 2Hz, C-4-H), 7.17 (1H, s, C-5-H), 7.45 (1H, s, C-8-H).

Laxanthone-II (2). Brownish-green ferric reaction and spectral data showed a chelated OH. It did not undergo methylation with CH₂N₂ indicating that it contained only a chelated OH. The two consecutive losses of 42 a.m.u. in its MS, showed the possibility of the presence of two acetoxyis functions. Further, hydrolysis of 2 with EtOH-HCl gave 2a which underwent methylation with CH₂N₂ to give a Me ether identical with 1a indicating that 2 was also a 1, 3, 6, 7-tetraoxygenated xanthone. Acetylation of 2 and 2a with Ac₂O-Py gave an acetate (2b) which was shown by PMR to contain one methoxyl and 3 acetoxyis. Hence, laxanthone-II had one methoxyl and two acetoxyis at the C-3, 6 and 7 positions whereas C-1 contained a chelated OH. Since the signals at δ 6.9 and 6.96 assigned to the *meta*-coupled protons had values lower than those noted in the case of 1a, 2b probably also had two acetoxyis functions at the C-1 and 3 positions as observed in the case of 1b. The remaining acetoxyis and methoxyl were placed at C-6 and 7 respectively on the basis of the following con-



1. R₁ = R₂ = H; R₃ = R₄ = Me
- 1a, R₁ = H; R₂ = R₃ = R₄ = Me
- 1b, R₁ = R₂ = COMe; R₃ = R₄ = Me
2. R₁ = H; R₂ = R₃ = COMe; R₄ = Me
- 2a, R₁ = R₂ = R₃ = H; R₄ = Me
- 2b, R₁ = R₂ = R₃ = COMe; R₄ = Me
3. R₁ = R₃ = R₄ = H; R₂ = Me
4. R₁ = R₂ = R₄ = H; R₃ = Me

siderations. The hydrolysis product (2a) and the acetate (2b) of laxanthone-II on comparisons with the synthetic isometric samples, were found to be different from 1, 6, 7-trihydroxyxanthone-3-methoxyxanthone (3) [10] and 1, 3, 7-trihydroxy-6-methoxyxanthone (4) [9] and their triacetates but identical with 1, 3, 6-trihydroxy-7-methoxyxanthone (2a) [10] and its triacetate. Furthermore laxanthone-II was considered to be 1-hydroxy-3, 6-diacetoxy-7-methoxyxanthone (2). 2, C₁₈H₁₄O₈; mp 180-1°; $\nu_{\text{max}}^{\text{KBr}}$ 3400 (OH), 1750, 1656 (conj. CO) cm⁻¹; $\lambda_{\text{max}}^{\text{MeOH}}$ 240, 300, 360 nm; + AlCl₃ 240, 270, 325, 380 nm. MS. 358 (M⁺), 316, 274, 259, 245, 231, 217 and 203. 2a, C₁₄H₁₀O₆; mp 304° (decomp). 2b, C₂₀H₁₆O₉; mp 191-2°; PMR (δ ; CDCl₃): 2.35 (6H, s, 2x-OAc), 2.47 (3H, s, C-1-OAc), 3.96 (3H, s, OMe), 6.9 (1H, *d*, *J* = 2Hz, C-2-H), 6.96 (1H, *d*, *J* = 2Hz, C-4-H), 7.48 (1H, s, C-5-H), 8.04 (1H, s, C-8-H).

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