

EXPERIMENTAL

Si gel (60–100 mesh) was used for column chromatography and Si gel G for TLC. All analytical samples were dried over P_2O_5 for 24 hr in *vacuo* and were tested for purity by TLC and MS. Molecular formulae are in agreement with elemental analyses. The UV spectra were recorded in 95% EtOH and the IR spectra in KBr discs. Except for the furan derivative, MS data are presented neglecting peaks of relative intensity less than 0.5%. The ^{13}C NMR spectrum was recorded in $CDCl_3$ soln using Varian CFT 20 instrument and the peaks are expressed in δ (ppm) with $\delta_{CDCl_3} = 76.9$ ppm downfield from TMS.

Isolation of 1a. Air-dried finely ground roots (1 kg) of *Berberis coriaria* Royle ex Lindl. were successively extracted with $CHCl_3$ and EtOH in Soxhlet apparatus for 72 hr. After removal of the solvents, the residues were stirred with 5% aq. citric acid for 6 hr, filtered, and the filtrate extracted several times with $CHCl_3$, the extract washed free of acid and dried. The residue was dissolved in $CHCl_3$, the combined $CHCl_3$ solubles chromatographed using petrol and mixtures of petrol/EtOAc as eluents in order of increasing polarity. The petrol/EtOAc (20:1) eluate on evaporation gave a light brown solid which crystallized from petrol/EtOAc in light pink stout needles (1) (0.02 g), mp 185°. MS: m/e (% abundance for over 50%) 298 (M^+ , 71.4), 280, 234, 219, 177, 164, 163 (98.6), 161, 145, 136, 135 (100), 117, 115, 108, 107, 106, 105, 91, 79, 78, 77 (62.9), 55, 53, 51 and 43.

Acetylation of 1. In the usual way gave the diacetate mp 141°, λ_{max} 243 and 290 (log ϵ 4.77 and 3.51) nm; ν_{max} 2900, 1750, 1672, 1225 cm^{-1} ; δ (ppm): 2.35 (6H, s; Ar- CH_3), 2.42 (6H, s; $-O-COCH_3$), 3.32 (4H, s; $-CO-CH_2-$), 7.01 (2H, d, J 9 Hz, Ar-H), 7.35 (2H, dd; J 9 Hz and 2 Hz, Ar-H); 7.70 (2H, d, J 2 Hz; Ar-H); m/e (%): 382 (M^+ , <1), 340, 323, 322, 298, 291, 290, 205, 188, 178, 177 (87.0), 164, 163 δ (98.3), 162, 161, 145, 136, 135 (100), 107, 78, 77, 45 and 43 (59.1).

Methylation of 1 with MeI/K_2CO_3 gave the dimethyl ether, mp 68°; λ_{max} 220, 250 and 320 (log ϵ 4.14, 4.60 and 3.07) nm; ν_{max} 2940, 2860, 1660 and 1580 cm^{-1} ; δ (ppm): 2.31 (6H, s; Ar- CH_3), 3.41 (4H, s; $-CO-CH_2-$), 3.91 (6H, s; Ar- OCH_3), 6.89 (2H, d, J 9 Hz; Ar-H); 7.29 (2H, dd, J 9 Hz and 2 Hz; Ar-H), 7.60

(2H, d, J 2 Hz; Ar-H); m/e (%): 326 (M^+ , 35.4), 177, 150, 149 (100), 134, 106, 105, 91 and 78.

Cyclization of the methyl ether was effected in $POCl_3$ under reflux for 6 hr. The product mp 110°; λ_{max} 295 and 330 (log ϵ 4.01 and 4.44) nm; ν_{max} 2935, 2860, 1607, 1502, 792 and 740 cm^{-1} ; δ (ppm): 2.38 (6H, s; Ar- CH_3), 3.89 (6H, s; Ar- OCH_3), 6.84 (2H, d, J 8.5 Hz; Ar-H), 7.01 (2H, multiplicity obscured by furan proton signals, Ar-H), 7.03 (2H, multiplicity obscured by preceding signals; furan protons), 7.79 (2H, s; Ar-H); m/e (%): 308 (M^+ , 1.5), 307, 292, 266, 265, 249, 235, 159, 154, 149, 146, 145, 133, 125, 116, 115, 105 and 91.

Acknowledgements—The authors thank Dr. B. C. Das, C.N.R.S., Gif-sur-Yvette, France, and Dr. G. F. Smith, The University of Manchester, U.K., for the mass spectra and Professor W. Herz, The Florida State University, U.S.A., and Dr. D. N. Roy, University of Toronto, Canada, for the PMR spectra.

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1-HYDROXY-3,7-DIMETHOXY-6-ACETOXYXANTHONE, A NEW XANTHONE FROM *LAWSONIA INERMIS*

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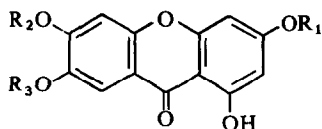
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(Received 9 January 1978)

Key Word Index—*Lawsonia inermis* (syn. *L. alba*); Lythraceae; xanthones; laxanthone-III; 1-hydroxy-3,7-dimethoxy-6-acetoxanthone.

Lawsonia inermis (syn. *L. alba*), well-known as a source of an orange dye [1] and for its medicinal uses [2], has been examined extensively for its chemical components [3–12]. The present communication describes the characterisation of a new xanthone, laxanthone-III. A solvent-free ethanolic extract of the whole plant (3 kg) was chromatographed over a Si gel column using a number of solvent systems. Elutions with petrol- C_6H_6 (7:3) gave laxanthone-III (1) whereas other fractions yielded compounds reported earlier. Colour reactions and spectral data for 1 indicated a chelated OH. On acetylation 1

gave a monoacetate (1a) but remained unchanged on methylation with CH_2N_2 in ether indicating that it had only one chelated OH. Hydrolysis of 1 yielded a dihydroxydimethoxy compound (1b) which underwent monoethylation to yield a monoethyl ether (1c), and also, methylation with CH_2N_2 in ether to give a monomethyl ether identical with 1-hydroxy-3,6,7-trimethoxyxanthone (1d) [13] showing that 1 like laxanthone-I (2) and II (3) was also a 1,3,6,7-tetraoxygenated xanthone. The NMR spectrum of 1 showed signals for two methoxys, one acetoxy, a pair of *m*-coupled and two other aromatic



- 1, $R_1 = R_3 = \text{Me}$; $R_2 = \text{Ac}$
 1d, $R_1 = R_2 = R_3 = \text{Me}$
 2, $R_1 = \text{H}$; $R_2 = R_3 = \text{Me}$
 3, $R_1 = R_2 = \text{Ac}$; $R_3 = \text{Me}$
 4, $R_3 = \text{H}$; $R_1 = R_2 = \text{Me}$
 5, $R_1 = R_3 = \text{H}$; $R_2 = \text{Me}$

protons. **1** could, thus, be a 1-hydroxy-3,6,7-acetoxy-dimethoxyxanthone. The positions of the two methoxys and one acetoxy substituents were fixed at C-3, C-6 and C-7 based on the following considerations. The hydrolysis product (**1b**) gave a Gibbs test characteristic for an unsubstituted position *para* to a hydroxyl [14, 15] but did not give a Quastel test indicating the absence of an *o*-dihydroxy system [16]. Moreover, **1b** on direct comparisons was found to be different from both 1,3-dihydroxy-6,7-dimethoxyxanthone (**2**) [13] and 1,7-dihydroxy-3,6-dimethoxyxanthone (**4**) (obtained by the selective methylation of **5** [13] but identical with 1,6-dihydroxy-3,7-dimethoxyxanthone (**1b**) [17] thereby locating the two methoxys at C-3 and C-7 positions in **1** and its derivatives. The structural assignments were further substantiated by the identity of the acetate of **1** with the synthetic diacetate (**1a**) but not with the isomeric diacetates, **2a** and **4a** [17]. Hence, laxanthone-III and the monoethyl ether of its hydrolysis were considered to be 6-*O*-acetyl (**1**) and 6-*O*-ethyl (**1c**) derivatives of **1b**. The structure of laxanthone-III is thus 1-hydroxy-3,7-dimethoxy-6-acetoxyxanthone.

EXPERIMENTAL

1. Light yellow needles from CHCl_3 -petrol: mp 210–211° (Found: C, 61.3; H, 4.6. $\text{C}_{17}\text{H}_{14}\text{O}_7$ requires: C, 61.32; H, 4.27%); $\nu_{\text{max}}^{\text{KBr}}$ 3100 (OH), 1775, 1650 (conj. CO) cm^{-1} ; $\lambda_{\text{max}}^{\text{MeOH}}$ 260, 305, 360 nm; + AlCl_3 265, 330, 405 nm; PMR (δ ; CDCl_3): 2.37 (3H, s, —OCOMe), 3.87 (3H, s, —OMe), 3.94 (3H, s, OMe), 6.37 (1H, d, $J = 2.5$ Hz, C-2-H), 6.42 (1H, d, $J = 2.5$ Hz, C-4-H), 7.19 (1H, s, C-5-H), 7.70 (1H, s, C-8-H) and 12.78 (—OH).

1a. Acetylation ($\text{Ac}_2\text{O/Py}$) of **1** gave **1a** colourless needles from CHCl_3 -petrol, mp 216–217° (Found: C, 61.4; H, 4.7.

$\text{C}_{19}\text{H}_{16}\text{O}_8$ requires: C, 61.29; H, 4.33%); PMR (δ , CDCl_3): 2.34 (3H, s, C-6-OCOMe), 2.46 (3H, s, C-1-OCOMe), 3.91 (6H, s, 2 \times OMe), 6.61 (1H, d, $J = 2.5$ Hz, C-2-H), 6.80 (1H, d, $J = 2.5$ Hz, C-4-H), 7.19 (1H, s, C-5-H), 7.78 (1H, s, C-8-H).

1b. Hydrolysis (EtOH/HCl) of **1** gave **1b**, light-yellow needles from EtOH, mp 264–265° (Found: C, 62.2; H, 4.4. $\text{C}_{15}\text{H}_{12}\text{O}_6$ requires: C, 62.5; H, 4.2%); treatment of **1b** in Et_2O with CH_2N_2 gave a methyl ether identical with 1-hydroxy-3,6,7-trimethoxyxanthone (**1d**) [13].

1c. Ethylation of **1b** with Et_2SO_4 (1 mole) KHCO_3 in Me_2CO gave **1c**, light-yellow needles from MeOH, mp 221–222° (Found: C, 64.5; H, 5.3. $\text{C}_{17}\text{H}_{16}\text{O}_6$ requires: C, 64.55; H, 5.1%).

4. Methylation of **5** [13] with Me_2SO_4 (1 mole)/ K_2CO_3 in Me_2CO gave **4**, mp 220–221° (Found: C, 62.8; H, 4.8. $\text{C}_{15}\text{H}_{12}\text{O}_6$ requires: C, 62.5; H, 4.2%).

Acknowledgements—The authors wish to thank the late Prof. T. R. Seshadri for his interest in this work, Prof. R. P. Singh, Head of the Chemistry Department, Delhi University for providing facilities, and the Council of Scientific and Industrial Research and University Grants Commission for grants.

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A NEW ISOFLAVONE FROM *IRIS KUMAONENSIS*

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(Revised received 21 January 1978)

Key Word Index—*Iris kumaonensis*; Iridaceae; iridin; iriskumaonin; veratric acid.

Iris kumaonensis Wall was found to contain, in addition to iridin [1], a crystalline product which upon close examination by TLC was a mixture of two glycosides. All attempts to separate the mixture failed; however,

acid hydrolysis followed by column chromatography over Si gel gave crystalline iriskumaonin, a new isoflavone, as one of the products. Elemental and MS analysis established the molecular formula $\text{C}_{18}\text{H}_{14}\text{O}_7$.