



- 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.

REFERENCES

- Rehsi, S. S. and Daruvala, E. D. (1957) *J. Sci. Ind. Res. (India)* **16**, 428.
- Dastur, J. E. (1962) *Medicinal Plants of India and Pakistan* p. 101. Taraporevala, D. B., Bombay (India).
- Agrawal, S. R., Ghatak, S. N. and Dhingra, D. R. (1959) *J. Indian Oil Soap* **25**, 145.
- Latif, A. (1959) *Indian J. Agr. Sci.* **29**, 147.
- Vishnevatskaya, S. G. (1962) *Maslob-Zhir, Prom.* **28**, 30.
- Kedlaya, K. J., Selvarangan, R. and Nayudamma, Y. (1963) *Leather Sci. (Madras, India)* **10**, 305.
- Machatzke, H., Vaughan, W. R., Charlotte, L. W. and White, G. R. (1957) *J. Pharm. Sci.* **56**, 86.
- Prasad, V. and Gupta, S. C. (1967) *Indian J. Exp. Biol.* **5**, 193.
- Lal, J. B. and Dutta, S. B. (1933) *J. Indian Chem. Soc.* **577**.
- Bhardwaj, D. K., Murari, R., Seshadri, T. R. and Singh, R. (1976) *Phytochemistry* **15**, 1789.
- Bhardwaj, D. K., Seshadri, T. R. and Singh, R. (1977) *Phytochemistry* **16**, 1616.
- Chakraborty, T., Podder, G. and Deshmukh, S. K. (1977) *Indian J. Chem.* **15B**, 96.
- Yates, P. and Stout, G. H. (1958) *J. Am. Chem. Soc.* **80**, 1691.
- Gibbs, H. D. (1927) *J. Biol. Chem.* **72**, 649.
- King, F. E., King, T. J. and Manning, L. C. (1957) *J. Chem. Soc.* **563**.
- Quastel, J. H. (1931) *Analyst* **56**, 311.
- Bhardwaj, D. K., Jain, R. K. and Mehta, C. K. (1978) *Indian J. Chem.* **16B** (under publication).

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 $\text{C}_{18}\text{H}_{14}\text{O}_7$.

PMR indicated an isoflavone nucleus with the absence of a chelated 5,2' or 6'-OH groups. This was confirmed by UV spectrum which also showed the absence of a 7-OH group. The two proton methylenedioxy peak at δ 6.16s was confirmed by a positive Labat test. It formed a methyl ether $C_{19}H_{16}O_7$, $KMnO_4$ oxidation of which gave veratric acid; this places two oxygen functions at 3' and 4' positions. The downfield shift of one -OMe (δ 4.15) shows its proximity to a carbonyl group and, therefore, places it at position C-5. The position of one H signal at δ 6.73s places one proton at C-8 and so the methylenedioxy group is at C-6,7. The compound formed a monoacetate, $C_{20}H_{16}O_8$, in the PMR of which there is no splitting in 5',6' protons which appear at almost the same position as in the original phenol. This fixes the position of the hydroxy at 3'. From the above data, the structure 3'-hydroxy-5,4'-dimethoxy-6,7-methylenedioxyisoflavone is proposed for iriskumao-nin.

EXPERIMENTAL

Isolation. MeOH extract of the powdered defatted whole plant of *Iris kumaonensis* (2 kg) on concentration deposited a pale greenish yellow solid which was hydrolysed by alcoholic 2% H_2SO_4 . The product was taken in $CHCl_3$ and after concentration deposited a solid. The mother liquor (1.5 g) was chromatographed over a Si gel column (100 g/100–200 mesh, 30×2.7 cm). Elution (solvent height 27 cm) was done with petrol: EtOAc (7:3, 60×50 ml and then 6:4, 60×50 ml). Fractions 63–114 (TLC pure) were pooled, evaporated to dryness and crystallized from EtOAc–petrol to give a silky solid (150 mg), mp $207-8^\circ$, UV: λ_{max}^{MeOH} 264 and 325 nm (sh), $+AlCl_3$ and $+NaOAc$ no

shift IR(KBr): 3250 (OH), 1640 ($>C=O$), 1529, 2155, 1206, 1178, 1110, 1060, 933 (O—CH₂—O), 872, 860, 816, 773 cm^{-1} etc., PMR (100 MHz, $CDCl_3$) δ : 7.88s (1H, 2-H), 7.36s (1H, 2'-H), 7.02s (2H, 5',6'-H), 6.73s (1H, 8-H), 6.16s (2H, O—CH₂—O), 5.79s (1H, 3'-OH), 4.15s (3H, 5-OCH₃) and 3.88s (3H, 4'-OCH₃); peak at δ 5.79 disappears on D_2O exchange (Found: C, 63.18; H, 4.2. Calculated for $C_{19}H_{14}O_7$: C, 63.21; H, 4.09%).

Acetylation. ($Ac_2O-C_5H_5N$) gave the monoacetate, crystallized from EtOAc–petrol into colourless needles, mp $176-177^\circ$, PMR (60 MHz, $CDCl_3$) δ : 7.84s (2-H), 7.34s (2'-H), 7.08s (5',6'-H), 6.65s (8-H), 6.08s (O—CH₂—O), 4.11s (5-OMe), 3.88s (4'-OMe) and 2.33s (3'-OCOCH₃), MS: M^+ 384, 342 (100%), 341, 324, 314, 313, 312, 311, 297, 296, 194, 179, 167, 166, 148 etc. (Found: C, 62.31; H, 4.08. Calculated for $C_{20}H_{16}O_8$: C, 62.5; H, 4.16%).

Methylation and oxidation. $Me_2SO_4-K_2CO_3$ -acetone, colourless crystalline solid mp $185-186^\circ$ (Found: C, 64.09; H, 4.52. Calculated for $C_{19}H_{16}O_7$: C, 64.04; H, 4.49%). 50 mg of this solid were oxidised by the procedure of Adinarayana and Rao [2] and the product (15 mg), mp $179.5-81.5^\circ$ showed PMR (100 MHz, $CDCl_3$) at δ : 7.71dd ($J = 8.5$ and 2 Hz, 1H, 6-H), 7.53d ($J = 2$ Hz, 1H, 2-H), 6.84d ($J = 8.5$ Hz, 1H, 5-H) and 3.86s (6H; 3,4-OCH₃), mmp and co-TLC with an authentic sample of veratric acid.

Acknowledgements—Our thanks are due to Dr. C. K. Atal for his interest in this work, Mr. E. A. Underwood, Exeter University, and Dr. Y. V. Subbarao, R. R. L., Hyderabad, for spectral data.

REFERENCES

1. Dhar, K. L. and Kalla, A. K. (1972) *Phytochemistry* **11**, 3097.
2. Adinarayana, D. and Rao, J. R. (1972) *Tetrahedron* **27**, 5377.

DALBINOL—A NEW 12a-HYDROXYROTENOID FROM *DALBERGIA LATIFOLIA* SEEDS

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(Received 13 January 1978)

Key Word Index—*Dalbergia latifolia*; Leguminosae; rotenoid; 12a-hydroxyamorphigenin.

Dalbergia latifolia, Indian Rosewood, is valued for its durable timber which is resistant to attack by insects and microorganisms. Its bark and heartwood have been chemically examined [1–4]; from its seeds, however, only sisafolin [5], a substituted 4-phenylcoumarin has been reported. The present communication deals with the structure elucidation of a new rotenoid from the seeds.

The air dried powdered seeds were exhaustively extracted with petrol, C_6H_6 and EtOH. The C_6H_6 concentrate was column chromatographed using Si gel. The EtOAc– C_6H_6 (1:9) eluates on concentration yielded a new 12a-hydroxyrotenoid, dalbinol. It analysed for $C_{23}H_{22}O_8$, mp $103-105^\circ$, $[\alpha]_D -42.80$ (c. 0.53, MeOH) and gave positive Durham's and Rogers Calamari tests suggesting a