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 6.16*s* 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 6.73*s* 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 iriskumaonin.

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°, UV: $\lambda_{\max}^{\text{MeOH}}$ 264 and 325 nm (sh), $+AlCl_3$ and +NaOAc no shift IR(KBr): 3250 (OH), 1640 ($\rangle C{=}O$), 1529, 2155, 1206, 1178, 1110, 1060, 933 ($O{-}CH_2{-}O$), 872, 860, 816, 773 cm^{-1} etc., PMR (100 MHz, $CDCl_3$) δ: 7.88*s* (1H, 2-H), 7.36*s* (1H, 2′-H), 7.02*s* (2H, 5′,6′-H), 6.73*s* (1H, 8-H), 6.16*s* (2H, $O{-}CH_2{-}O$), 5.79*s* (1H, 3′-OH), 4.15*s* (3H, 5-OCH_3) and 3 88*s* (3H, 4′-OCH_3); peak at δ 5.79 disappears on D_2O exchange (Found: C, 63.18; H, 4.2. Calculated for $C_{18}H_{14}O_7$: 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°, PMR (60 MHz, $CDCl_3$) δ: 7.84*s* (2-H), 7.34*s* (2′-H), 7.08*s* (5′,6′-H), 6.65*s* (8-H), 6.08*s* ($O{-}CH_2{-}O$), 4.11*s* (5-OMe), 3.88*s* (4′-OMe) and 2.33*s* (3′-$OCOCH_3$), 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° (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° showed PMR (100 MHz, $CDCl_3$) at δ: 7.71*dd* ($J = 8.5$ and 2 Hz, 1H, 6-H), 7.53*d* ($J = 2$ Hz, 1H, 2-H), 6.84*d* ($J = 8.5$ Hz, 1H, 5-H) and 3.86*s* (6H; 3,4:OCH_3), mmp and co-TLC with an authentic sample of veratric acid.

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REFERENCES

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

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

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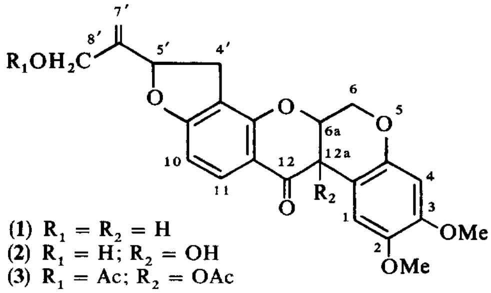
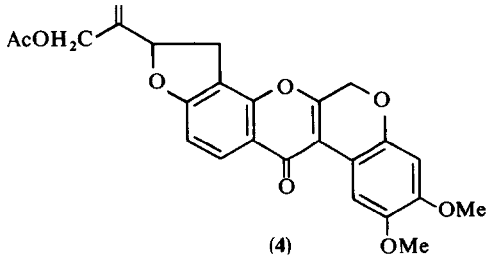
Key Word Index—*Dalbergia latifolia*; Leguminosae; rotenoid; 12a-hydroxyamorphigenin.

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°, $[\alpha]_D$ −42.80 (*c*, 0.53, MeOH) and gave positive Durham's and Rogers Calamari tests suggesting a



(1) $R_1 = R_2 = H$
(2) $R_1 = H$; $R_2 = OH$
(3) $R_1 = Ac$; $R_2 = OAc$



(4)

rotenoid skeleton. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3490 (–OH), 1675 (12-carbonyl); UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 235 (4.29), 242 *sh* (4.24) and 292 (4.36). UV and IR spectra of the compound showed close resemblance to those reported for amorphin and amorphigenin (1)[6] thus indicating a strucutral similarity.

Dalbinol (2) on warming with conc H_2SO_4 and HOAc gave a yellow compound (4), mp 177–178°; IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1739 (acetate), 1634 (12-carbonyl): UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 235 (4.36), 280 (4.26), 310 (4.17); NMR (60 MHz, $CDCl_3$): δ 2.15 (3H, *s*, aliphatic –OAc), 3.82, 3.91 (2 × 3H, each *s*, 2 × –OMe), 3.40 (2H, *m*, C-4′), 4.71 (protons α to 8′-acetoxyl), 4.94 (2H, *s*, C-6), 5.29, 5.38 (2H, C-7′), 5.36 (1H, *m*, C-5′), 6.44 (1H, *s*, C-4), 6.82 (1H, *d*, $J_{10,11} = 9$ Hz, C-10), 7.92 (1H, *d*, $J_{10,11} = 9$ Hz, C-11) and 8.30 (1H, *s*, C-1). **4** was identified as 8′-acetoxy-6a,12a-dehydro-amorphigenin on the basis of above data and comparison of these data with those reported from amorphigenin.

Dalbinol on acetylation with Ac_2O–Py formed a diacetate (3), mp 80°; IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1736 (acetate), 1675 (12-carbonyl): NMR (60 MHz, $CDCl_3$): δ 2.12, 2.20 (2 × 3H, each *s*, 2 × aliphatic –OAc), 3.44 (2H, *m*, C-4′), 3.68, 3.72 (2 × 3H, each *s*, 2 × –OMe), 3.82–5.00 (3H, *m*, C-6, C-6a), 4.35 (2H, protons α to 8′-acetoxyl), 5.16, 5.22 (2H, C-7′), 5.34 (1H, *m*, C-5′), 6.34 (1H, *s*, C-4), 6.40 (1H, *d*, $J_{10,11} = 9$ Hz, C-10), 6.79 (1H, *s*, C-1) and 7.62 (1H, *d*, $J_{10,11} = 9$ Hz, C-11). It follows that dalbinol is similar to amorphigenin except that it contains an extra hydroxyl group which was eliminated in the formation of **4**. As the tertiary hydroxyl at 12a-position in the rotenoids is known to undergo easy dehydration [7, 8] giving rise to the corresponding dehydro product, so the second hydroxyl in dalbinol can be assigned the 12a-position. The dehydration leading to the formation of a double bond at 6a,12a-position was accompanied by characteristic shift of 12-keto peak to 1634 cm^{-1}. The downfield shift of 1-proton from δ 6.56 in dalbinol to δ 8.30 in dehydro compound was observed as the 1-proton is now more efficiently negatively shielded by the 12-carbonyl as it is more nearly in plane. The doublets due to 10- and 11-protons are also shifted downfield to δ 6.82 and 7.92 from 6.42 and 7.70 in dalbinol. The multiplet due to the 6,6a- and 12a-hydroxyl protons contracted to a sharp two proton band at δ 4.94 due to the 6-methylene in **4**.

Thus dalbinol is (–)-12a-hydroxyamorphigenin (2), a structure confirmed by its mass spectrum which showed a base peak at *m/e* 408 corresponding to M-18 value showing that dehydration had occurred. Although it does not show the molecular ion peak, the two RDA fragments at *m/e* 208 and 219 add up to the calculated (M + 1) value. The peak at *m/e* 208 appears as an abundant and intense peak and is a distinguishing feature of 12a-hydroxyrotenoids having the 2,3-dimethoxychroman system [9].

REFERENCES

1. Dhingra, V. K., Mukherjee, S. K., Saroja, T. and Seshadri, T. R. (1971) *Phytochemistry* **10**, 2551.
2. Balakrishna, S., Rao, M. M. and Seshadri, T. R. (1962) *Tetrahedron* **18**, 1503.
3. Rao, M. M. and Seshadri, T. R. (1963) *Tetrahedron Letters* 211.
4. Kumari, D., Mukherjee, S. K. and Seshadri, T. R. (1965) *Tetrahedron* **21**, 1495.
5. Saxena, V. K., Tiwari, K. P. and Tandon, S. P. (1970) *Proc. Natl. Acad. Sci. (India)* **40A**, 165.
6. Claisse, J., Crombie, L. and Peace, R. (1964) *J. Chem. Soc.* 6023.
7. Krishnamurti, M., Sambhy, Y. R. and Seshadri, T. R. (1970) *Tetrahedron* **26**, 3023.
8. Sarma, P. N., Srimannarayana, G. and Subba Rao, N. V. (1976) *Indian J. Chem.* **14B**, 152.
9. Ollis, W. D., Rhodes, C. A. and Sutherland, I. O. (1967) *Tetrahedron* **23**, 4741.