epoxide ring), 3·37 δ (*m*, H-3), 3·70 δ (*m*, H-7), 3·97 δ (s, C$\underline{H}_2$OAc). The product was also prepared by treatment of *iso*-linearol with *p*-nitroperbenzoic acid, as described for similar derivatives [4].

Iso*linearol*. The NMR spectrum, recorded in $CDCl_3$, gave the following signals: 0·76 and 1·05 δ (s, *t*, Me), 1·71 δ (*d*, *J* 1·5 Hz, allylic Me), 2·07 δ (s, OCOMe), 3·37 δ (*m*, H-3), 3·65 δ (*m*, H-7), 3·99 δ (s, C$\underline{H}_2$OAc), 5·48 δ (broad s, H-15). Small differences are therefore noted in comparison with the spectrum in DMSO-d_6 [2, 3].

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REFERENCES

1. Piozzi, F., Venturella, P., Bellino, A. and Mondelli, R. (1968) *Tetrahedron* **24**, 4073.
2. De Quesada, T. G., Rodriguez, B., Valverde, S. and Huneck, S. (1973) *Anal. Quim.* **69**, 767.
3. De Quesada, T. G., Rodriguez, B., Valverde, S. and Huneck, S. (1972) *Tetrahedron Letters* 2187.
4. Piozzi, F., Venturella, P., Bellino, A. and Mondelli, R. (1968) *Ric. Sci. (Rome)* **38**, 462.

Phytochemistry, 1975, Vol. 14, pp. 1452–1453. Pergamon Press. Printed in England.

FLAVONOIDS FROM *DALBERGIA CEARENSIS**

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Key Word Index—*Dalbergia cearensis*; Leguminosae; neoflavonoids; isoflavonoids; 2,5-dihydroxy-4-methoxybenzophenone.

Herbarium samples of *Dalbergia cearensis* Ducke and *D. frutescens* (Vell.) Britt. (= *D. variabilis* Vog.) are very similar. In the field, however, the species are easily distinguished, since *D. cearensis* is a tree and *D. frutescens* a scandent shrub [2]. The present phytochemical examination is based on a sample of trunk wood, collected by Dr. F. J. de Abreu Matos, Universidade Federal do Ceará, a former collaborator of Dr. A. Ducke, at Acaraú, Ceará State, from a small tree (height 4·5 m, diameter of heartwood 9 cm). The correctness of the identification was confirmed by Dr. D. de Andrade Lima, Universidade Federal de Pernambuco, by comparison of herborized material. Among the seven compounds isolated, (*S*)-4-methoxydalbergione [3], dalbergin [4], formononetin [1], and (±)-demethylhomopterocarpin [1] had already been obtained from other species during the current study of *Dalbergia* and *Machaerium*, and were identified by direct comparison with authentic samples.

One of the additional compounds was identical in all respects to (*S*)-mucronulatol [5, 6] with exception of the antipodal ORD curve and must thus represent the, as yet unreported, (*R*)-mucronulatol (**1a**). The racemate of mucronulatol occurs in *D. frutescens* [5].

Careful analysis of the τ 5·3–5·9 region [7] of the PMR spectrum (τ 5·32, H_{eq}-2; 5·50 H_{ax}-2; 5·81, H-3) revealed still another compound $C_{15}H_8O_2 \cdot OH(OMe)_3$, to be isoflavanone (**2a**). Retroaldol cleavage led to MS peaks compatible with monohydroxylation of ring *A* and trimethoxylation of ring *B*. The typical aromatic ABX PMR pattern, which included a low field d (τ 2·1, *J* 8·5 Hz), and UV NaOAc shifts placed the OH at C-7. One of the ring *B* hydrogens is situated at a relatively deprotected site (τ 3·00, *J* 8·5 Hz), vicinal to the other (τ 3·20, *J* 8·5 Hz) hydrogen. This evidence is in good agreement with the structure of 3′-*O*-methylvio-

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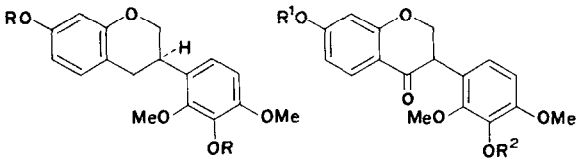
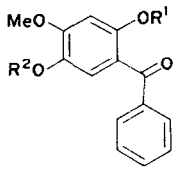


(1a) R = H
(1b) R = Me
(1c) R = Ac

(2a) R^1 = H, R^2 = Me
(2b) R^1 = R^2 = Me
(2c) R^1 = R^2 = H



(3a) R^1 = R^2 = H
(3b) R^1 = H, R^2 = Me
(3c) R^1 = R^2 = Me

lanone (**2a**), which thus shares with mucronulatol (**1a**) the oxygenation pattern of the aromatic rings. The only ring *B* alternative would sustain one of the vicinal protons at C-4', a highly improbable situation from the biosynthetic point of view. Violanone (**2c**) [8] occurs in *Dalbergia miscolobium* Benth. [= *D. violacea* (Vog.) Malme].

IR, PMR and MS for cearoin, $C_{13}H_7O(OH)_2OMe$, the remaining additional compound, are consistent with 2,4-dihydroxy-5-methoxy- and 2,5-dihydroxy-4-methoxybenzophenone (**3a**) structures. Cearoin, however, is easily oxidized by air in alkaline solution, a fact which is compatible with the *para*-relation of two phenolic hydroxyls. Indeed, the mps of synthetic **3a** and **3b** [9] are identical with the mps respectively of cearoin and its monomethyl ether.

EXPERIMENTAL

Isolation of the constituents of D. cearensis. The powdered softwood (5 kg) was extracted with C_6H_6. The extract (41 g) was chromatographed on a silica (800 g) column giving the following fractions with the indicated eluants: C_6H_6 (A_1, A_2, A_3, A_4), C_6H_6–$CHCl_3$ 8:2 (A_5, A_6, A_7). A_1 was recrystallized from EtOH affording *S-4-methoxydalbergione* (23 mg). A_2 was recrystallized from Me_2CO affording **3a** (150 mg). A_3 was recrystallized from C_6H_6–MeOH affording (±)-*demethylhomopterocarpin* (65 mg). A_4 was fractionally crystallized from EtOH giving *dalbergin* (112 mg). A_5 was recrystallized successively from various solvents and EtOH affording **1a** (47 mg). A_6 was washed with C_6H_6 and crystallized from C_6H_6–MeOH affording **2a** (124 mg). A_7 was purified by rechromatography (SiO_2, C_6H_6–$CHCl_3$ 8:2) and recrystallization from C_6H_6–MeOH afforded *formononetin* (234 mg).

(3*R*)-7,3'-*Dihydroxy*-2',4'-*dimethoxyisoflavan* [(*R*)-mucronulatol] (**1a**), cream-coloured crystals, mp 147–149° (EtOH) (found: C, 67·41; H, 5·85. $C_{17}H_{18}O_5$ requires: C, 67·54; H, 6·00%). λ_{max}^{EtOH} (nm): 225, 282 (ε 16900, 9700); no NaOAc, H_3BO_3 + NaOAc, $AlCl_3$ shifts; $\lambda_{max}^{EtOH+NaOH}$ (nm): 246, 292 (ε 16900, 10800). ν_{max}^{KBr} (cm^{-1}): 3348, 1623, 1592, 1497, 1439, 1330, 1289, 1232, 1205, 1156, 1112, 1093, 1033, 1027, 901, 885, 807. PMR [$(CD_3)_2CO$, τ]: 1·93 (*s*, OH), 2·59 (*s*, OH), 3·17 (*d*, *J* 7·0 Hz, H-5), 3·29 (*d*, *J* 8·0 Hz, H-6'), 3·40 (*d*, *J* 8·0 Hz, H-5'), 3·63 (*dd*, *J* 7·0, 2·0 Hz, H-6), 3·73 (*d*, *J* 2·0 Hz, H-8), 5·85 (*dd*, *J* 9·0, 4·0 Hz, H-2_{eq}), 6·03–6·23 (superimp. by OMe-signals, H-2_{ax}), 6·13 (*s*, OMe), 6·19 (*s*, OMe), 6·35–6·85 (*m*, H-3), 7·15 (*d*, *J* 8·0 Hz, 2 H-4). MS (*m/e*): 302 (71%) M, 180 (100), 168 (63), 167 (33), 150 (15). ORD (*c* 1·05 mg/ml, MeOH, 230–440 nm): $[\phi]_{400}$ + 570, $[\phi]_{308}$ +1400, $[\phi]_{290}^{pk}$ +3850, $[\phi]_{278}$ 0, $[\phi]_{270}$ −3140, $[\phi]_{250}$ −5740, $[\phi]_{238}$ −9650. *Dimethyl ether* (**1b**) (**1a**, Me_2SO_4, K_2CO_3, Me_2CO, reflux, 8 hr), mp 73–74° (MeOH). MS (*m/e*): 330 (62%) M, 195 (13), 194 (100), 182 (37), 181 (23), 179 (46), 151 (16), 149 (20), 136 (10). *Diacetate* (**1c**) mp 126–128°.

7-*Hydroxy*-2',3',4'-*trimethoxyisoflavanone* (**2a**), colourless crystals, mp 192–194° (C_6H_6–MeOH) (found: C, 65·64; H, 5·57. $C_{18}H_{18}O_6$ requires: C, 65·45; H, 5·49%). λ_{max}^{MeOH} (nm): 208, 227, 276, 315 (ε 82500, 36300, 29700, 21450); $\lambda_{max}^{MeOH+NaOAc}$ (nm): 215, 284, 337 (ε 70100, 21450, 33750). ν_{max}^{KBr} (cm^{-1}): 3333, 1661, 1587, 1490, 1460, 1259, 1236, 1215, 1193, 1163, 1100, 1022, 1012, 858, 800. PMR [$(CD_3)_2CO$, τ]: 2·10 (*d*, *J* 8·5 Hz, H-5), 3·00 (*d*, *J* 8·5 Hz, H-6'), 3·20 (*d*, *J* 8·5 Hz, H-5'), 3·30 (*dd*, *J* 8·5 Hz, H-6), 3·47 (*d*, *J* 2·5 Hz, H-8), 5·32 (*dd*, *J* 12·0, 5·0 Hz, H_{eq}-2), 5·5 (*t*, *J* 12·0 Hz, H_{ax}-2), 5·81 (*dd*, *J* 12·0, 5·0 Hz, H_{ax}-3), 6·15 (*br s*, 3 Me). MS (*m/e*): 330 (25%) M, 194 (100), 195 (15), 179 (25), 136 (8). *Methyl ether* (**2b**) (**2a**, CH_2N_2, Et_2O), mp 133–135° (EtOH).

2,5-*Dihydroxy*-4-*methoxybenzophenone* (cearoin) (**3a**), yellow crystals, mp 187–188° (EtOH) [lit. [9] mp 188°] (found: C, 68·58; H, 4·89. $C_{14}H_{12}O_4$ requires: C, 68·85; H, 4·95%). $\nu_{max}^{CHCl_3}$ (cm^{-1}): 3448, 1645, 1265, 1120, 880. PMR ($CDCl_3$, τ): −2·38 (*s*, OH), 2·25–2·65 (*m*, C_6H_5), 2·88 (*s*, H-6), 3·43 (*s*, H-3), 4·80 (*s*, OH), 6·03 (*s*, Me). MS (*m/e*): 244 (100%) M, 243 (15) M-1, 167 (95), 166 (12), 105 (28), 77 (19). 5-*O-Methyl ether* (**3b**) (**3a**, Me_2SO_4 1 equiv., K_2CO_3, Me_2CO, reflux 2 h) mp and lit. [9] mp 106–107° (EtOH). PMR ($CDCl_3$, τ): −2·65 (*s*, OH), 2·20–2·45 (*m*, C_6H_5), 2·91 (*s*, H-6), 3·37 (*s*, H-3), 6·05 (*s*, Me), 6·32 (*s*, Me). 2,5-*Di-O-methyl ether* (**3c**) (**3a**, Me_2SO_4 excess, K_2CO_3, Me_2CO, reflux 6 hr). PMR ($CDCl_3$, τ): 2·10–2·65 (*m*, C_6H_5), 2·94 (*s*, H-6), 3·40 (*s*, H-3), 6·04 (*s*, Me), 6·15 (*s*, Me), 6·36 (*s*, Me).

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REFERENCES

1. Abreu Matos, F. J. de, Gottlieb, O. R. and Souza Andrade, C. H. (1975) *Phytochemistry* **14**, 825.
2. Ducke, A. (1959) *Anais Acad. brasil. Ciênc.* **31**, 211.
3. Eyton, W. B., Ollis, W. D., Sutherland, I. O., Gottlieb, O. R., Taveira Magalhães, M. and Jackman, L. M. (1965) *Tetrahedron* **21**, 2683.
4. Eyton, W. B., Ollis, W. D., Fineberg, M., Gottlieb, O. R., Salignac de Souza Guimarães, I. de and Taveira Magalhães, M. (1965) *Tetrahedron* **21**, 2697.
5. Kurosawa, K., Ollis, W. D., Redman, B. T., Sutherland, I. O., Braga de Oliveira, A., Gottlieb, O. R. and Magalhães Alves, H. (1968) *Chem. Commun.* 1263.
6. Kurosawa, K., Ollis, W. D., Redman, B. T., Sutherland, I. O., Gottlieb, O. R. and Magalhães Alves, H. (1968) *Chem. Commun.* 1265.
7. Viegas Assumpção, R. M. and Gottlieb, O. R. (1973) *Phytochemistry* **12**, 1188.
8. Ollis, W. D. (1968) *Recent Advances in Phytochemistry* (Mabry, T. J., Alston, R. E. and Runeckles, V. C., Eds.), Vol. 1, p. 360. Appleton–Century–Crofts, New York.
9. Laumas, K. R., Neelakantan, S. and Seshadri, T. R. (1957) *Proc. Indian Acad. Sci.* **46A**, 343; *Chem. Abstr.* **52**, 14570.