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FLAVONOIDS FROM *DALBERGIA ECASTOPHYLLUM**

FRANCISCO J. DE ABREU MATOS,† OTTO R. GOTTLIEB and CARLOS H. SOUZA ANDRADE†

Instituto de Química, Universidade de São Paulo, Brasil

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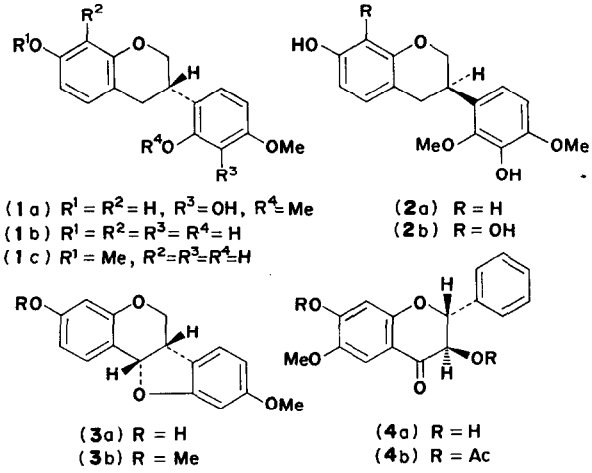
Dalbergia ecastophyllum (L.) Taub. (Leguminosae-Lotoideae) is a shrub which occurs along the sea and river shores of tropical America and Africa. A wood sample, collected in Nigeria, contained anethole, estragole, sitosterol, formononetin, (±)-mucronulatol (**1a**, **2a**) and (3*R*)-8-de-*O*-methylduartin (**2b**) [3]. From another sample, collected near Aquiraz, Ceará State, Brasil, 10 compounds were isolated. Among these, sitosterol, isoliquiritigenin [4], (2*S*)-liquiritigenin [5], formononetin [4], daidzein [4], (±)- and (6a*S*,11a*S*)-demethylhompterocarpin (**3a**) [6], as well as (3*S*)-vestitol (**1b**) [7, 8], had already been obtained from other species during the current study of the genera *Dalbergia* and *Machaerium*, and were identified by direct comparison with authentic samples.

UV, MS and PMR data classified one of the additional compounds, $C_{15}H_{11}O_2 . OH(OMe)_2$, as an *O*-methylvestitol (**1c**). The identification was confirmed by synthesis of the compound through diazomethane methylation of (3*S*)-vestitol (**1b**). The reaction was expected to have taken place at the less hindered hydroxyl of vestitol, settling the relative positions of the hydroxyl and the methoxyls in the natural *O*-methylvestitol. A more rigorous proof of the structure was achieved by its synthesis through hydrogenolysis of (6a*S*,11a*S*)-homopterocarpin (**3b**). Both samples of synthetic *O*-methylvestitol gave ORD curves which were superimposable on the analogous curve of the natural compound. This can consequently be formulated as (3*S*)-2′-hydroxy-7,4′-dimethoxyisoflavan (**1c**).



A 3-hydroxyflavanone structure with the substituents situated on ring *A* (**4a**) was deduced for the remaining compound $C_{15}H_9O_2(OH)_2OMe$, in view of its UV, MS and PMR (including the characteristic *AB*-signal [9]: τ 4·85, 5·50, two *d*, *J* 10·0 Hz). The decision concerning the relative positions of the hydroxyl and the methoxyl at C-6 and C-7 was made comparing the PMR spectra of the compound and of its diacetate. In contrast to a small paramagnetic shift of the H-5 signal, a comparatively much larger shift of the H-8 signal was noted. This indicated, of course, that a hydroxyl at the vicinal C-7 position had been acetylated (**4b**). As expected, upon acetylation the *B* part of the original *AB*-signal had undergone considerable paramagnetic shift (1·3 ppm), confirming the assignment of a secondary alcohol function to the 3-position. The 2*R*,3*R*-configuration for the natural

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† Departamento de Quimica Orgânica e Inorgânica, Universidade Federal do Ceará, Fortaleza.

product **4a**, was indicated upon comparison of its ORD curve with analogous data of representative 3-hydroxyflavanones [10].

The constituents of *D. ecastophyllum* can be placed in a biosynthetic series: chalcone → isoflavone → pterocarpan → isoflavan, on which comments are available [11].

EXPERIMENTAL

Isolation of the constituents of D. ecastophyllum. The powdered wood (9·6 kg) was successively extracted with C_6H_6 and EtOH. The C_6H_6 extract (87·5 g), suspended in C_6H_6, was poured on a SiO_2 (800 g) column. The column was percolated successively with C_6H_6, $CHCl_3$ and MeOH. The C_6H_6 soln was concentrated. The crystalline ppt was separated by filtration. Fractional recrystallizations from C_6H_6–MeOH yielded in the first crops **3a** (4·2 g) and in the last crops (±)-demethylhomopterocarpin (8 mg). The filtrate was evaporated and the residue (20 g) was chromatographed on SiO_2 (400 g), giving the following fractions with the indicated eluants: light petrol.–C_6H_6, 1:1 (A_1), C_6H_6 (A_2, A_3), C_6H_6–$CHCl_3$, 1:1 (A_4), $CHCl_3$ and $CHCl_3$–MeOH, 1:1 (A_5). A_1, A_2 and A_5: no component isolated. A_3 was washed with C_6H_{14} and recrystallized from MeOH affording *sitosterol* (30 mg). A_4 was crystallized from C_6H_6 and recrystallized from C_6H_6–MeOH affording **1c** (70 mg). The $CHCl_3$ soln was evaporated and the residue (20 mg) was chromatographed on SiO_2 (500 g), giving the following fractions with the indicated eluants: light petrol. (B_1), light petrol.–C_6H_6, 1:1 (B_2), C_6H_6 (B_3), C_6H_6–AcOEt, 95:5 (B_4, B_5), AcOEt (B_6). B_1, B_3 and B_6: no component isolated. B_2 (56 mg): *aliphatic ester*. B_4 was washed with light petrol. and recrystallized from MeOH affording **3a** (132 mg). B_5 was recrystallized from C_6H_6–MeOH affording **4a** (50 mg). In the MeOH crystallization liquors the presence of *daidzein* was demonstrated by TLC.

The EtOH extract (560 g) was extracted successively with C_6H_6 and $CHCl_3$. The C_6H_6 soln was evaporated. The residue (17 g) was chromatographed on SiO_2 (500 g), giving the following fractions with the indicated eluants: C_6H_6–$CHCl_3$, 1:1 (C_1), C_6H_6–$CHCl_3$, 2:8 (C_2), $CHCl_3$ (C_3), $CHCl_3$–MeOH, 99:1 (C_4, C_5), $CHCl_3$–MeOH, 98:2 (C_6). C_2 and C_6: no component isolated. C_1 was washed with C_6H_6 and recrystallized from MeOH affording **4a** (12 mg). C_3 was washed with C_6H_6 affording *formononetin* (65 mg). C_4 was recrystallized from C_6H_6–MeOH affording **2b** (40 mg). C_5 was purified by thick layer chromatography, yielding isoliquiritigenin (2 mg). The $CHCl_3$ soln was evaporated. The residue (5 g) was chromatographed on SiO_2 (150 g), giving the following fractions with the indicated eluants: $CHCl_3$ (D_1), $CHCl_3$–MeOH, 99:1 (D_2, D_3), $CHCl_3$–MeOH, 99:5 (D_4). D_1 and D_4: no component isolated. D_2 was washed with C_6H_6 affording *isoliquiritigenin* (8 mg). D_3 was recrystallized from EtOH affording (2*S*)-*liquiritigenin* (9 mg).

(3*S*)-*2′-Hydroxy-7,4′-dimethoxyisoflavan* (**1c**), colourless crystals, mp 153–155° (Found: C, 71·38; H, 6·30. $C_{17}H_{18}O_4$ requires: C, 71·31; H, 6·34%). λ_{max}^{EtOH} (nm): 228, 285 (ε 14000, 5200). ν_{max}^{KBr} (cm^{-1}): 3571, 3030, 2941, 1629, 1590, 1534, 1515, 1460, 1267, 1111, 943, 930, 845, 833, 807, 705, 725, 690. PMR [$(CD_3)_2CO$, τ]: 2·98 (*d*, *J* 8 Hz, H-5); 3·06 (*d*, *J* 7 Hz, H-6′); 3·51 (*d*, *J* 2 Hz, H-8); 3·64 (*dd*, *J* 8, 2 Hz, H-6); 3·58 (*dd*, *J* 7, 2 Hz, H-5′); 3·7 (*d*, *J* 2 Hz, H-3′); 5·5–6·0 (*m*, 2 H-2); 6·31 (*s*, 2 OMe); 6·8–7·2 (*m*, H-3, 2 H-4). MS (*m/e*): 286 (50%) M, 150 (68), 149 (31), 137 (100). ORD (*c* 0·145 mg/ml, MeOH): $[\phi]_{284}^{tr}$ −2760, $[\phi]_{278}$ 0, $[\phi]_{270}$ +1980, $[\phi]_{260}$ +2360, $[\phi]_{236}$ +11050. The compound was also obtained by methylation (CH_2N_2, Et_2O) of **1b**; as well as by methylation (Me_2SO_4, K_2CO_3, Me_2CO) of **3a** to **3b**, and hydrogenolysis (H_2, Pd/C, MeOH) of **3b**.

(2*R*,3*R*)-*3,7-Dihydroxy-6-methoxyflavanone* (**4a**), colourless crystals, mp 204–206° (Found: C, 66·80; H, 4·85. $C_{16}H_{14}O_5$ requires: C, 67·13; H, 4·93%). λ_{max}^{EtOH} (nm): 214, 240, 280 (ε 20400, 9700, 6000). ν_{max}^{KBr} (cm^{-1}): 3333, 2980, 1653, 1616, 1613, 1515, 1471, 1290, 1111, 990, 870, 785, 750, 690. PMR [$(CD_3)_2CO$, τ]: 2·60 (*br s*, C_6H_5), 2·70 (*s*, H-5), 3·54 (*s*, H-8), 4·85 (*d*, *J* 10·0 Hz, H-2), 5·50 (*d*, *J* 10·0 Hz, H-3), 6·10 (*s*, OMe). MS (*m/e*): 286 (30%) M, 167 (100), 151 (9), 120 (15), 105 (9), 91 (30). ORD (*c* 0·0638 mg/ml, MeOH): $[\phi]_{368}$ +2690, $[\phi]_{352}^{pk}$ +7670, $[\phi]_{347}$ 0, $[\phi]_{328}^{tr}$ −35860, $[\phi]_{305}$ 0, $[\phi]_{284}^{pk}$ +18830, $[\phi]_{268}^{tr}$ +16140, $[\phi]_{248}$ +20100. *Diacetate* (**4b**), oil. PMR (CCl_4, τ): 2·60 (*s*, C_6H_5, H-5), 3·23 (*s*, H-8), 4·23 (*s*, *J* 10·0 Hz, H-3), 4·70 (*s*, *J* 10·0 Hz, H-2), 6·10 (*s*, OMe), 7·60 (*s*, $MeCO_2Ar$), 8·00 (*s*, $MeCO_2R$).

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