oxidation was allowed to take place at room temp. for 60 hr. Aliquots (5 ml) were withdrawn in duplicate from the reaction mixture at different times and analysed for periodate and formic acid.

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(2*R*,3*S*,4*S*)-3,4,7,3′,4′-PENTAMETHOXY-2,3-*TRANS*-3,4-*CIS*-FLAVAN, A NOVEL FLAVAN FROM *NEORAUTANENIA AMBOENSIS*

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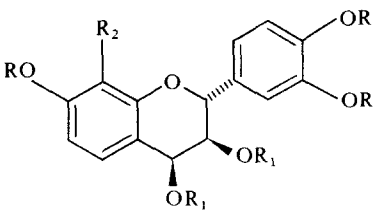
Key Word Index—*Neorautanenia amboensis;* Leguminosae; [2*R*,3*S*,4*S*]-leucofisetinidin; (+)-7,3′,4′-trihydroxy-2,3-*trans*-flavan-3,4-*cis*-diol; (+)-7,3′,4′-trimethoxy-2,3-*trans*-flavan-3,4-*cis*-diol; (+)-3,4,7,3′,4′-pentamethoxy-2,3-*trans*-3,4-*cis*-flavan.

Recent investigations [1–3] of the root bark of *Neorautanenia amboensis* Schinz revealed the presence of an exceptionally complex mixture of over 50 flavonoid compounds (mainly isoflavonoids), including rotenoids, pterocarpans, a pterocarpan-6a-ol, a pterocarpene, an isoflavan-4-ol, isoflavanones, isoflavones, a 3-phenylcoumarin, benzofurans and coumarins. We now report that examination of the methanol-soluble extractives resulted in the isolation and characterization of the leucofisetinidin **1**, (+)-7,3′,4′-trihydroxy-2,3-*trans*-flavan-3,4-*cis*-diol, and two new natural products*, (+)-7,3′,4′-trimethoxy-2,3-*trans*-flavan-3,4-*cis*-diol **2** and (+)-3,4,7,3′,4′-pentamethoxy-2,3-*trans*-3,4-*cis*-flavan **3**, with identical absolute configurations.

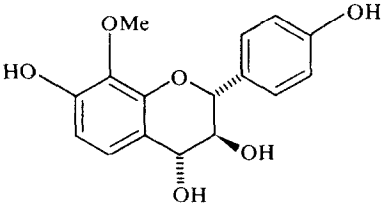
These new products represent different degrees of methylation of leucofisetinidin **1** with the unprecedented phenomenon in **3** where the equivalent of the 3,4-diol function is fully methylated. The isolation of **1**–**3** also represents the first observation of flavonoids associated with the predominant isoflavonoids in the *Neorautanenia* family; their origins being speculatively attributed to a common intermediate along the biogenetic pathway. This, together with the high degree of methylation of isoflavonoids present in the same source, probably explains the occurrence of flavans **2** and **3**.

Initial separation of components in the methanol extract was achieved through countercurrent distribution H_2O–butan-2-ol–*n*-hexane, 5:4.5:0.5 followed by chromatography on Si gel (C_6H_6–*n*-hexane–EtOAc, in 1:1:0.1). Final separations were done by preparative TLC and crystallization.

* Satisfactory analytical, spectroscopic and mass spectrometric data have been obtained.



1 R = R_1 = R_2 = H
2 R_1 = R_2 = H; R = Me
3 R_2 = H; R = R_1 = Me
4 R_2 = H; R = Me; R_1 = Ac
5 R = R_1 = H; R_2 = OMe

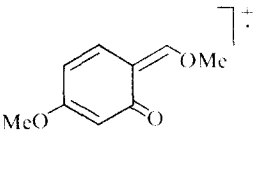


6

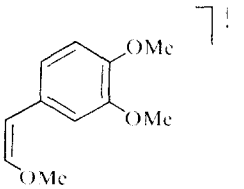
Leucofisetinidin **1**, R_f 0.57 (2% HOAc), has a NMR spectrum consistent with the proposed structure and was identified by conversion into fisetinidin chloride (flavylium-3,7,3′,4′-tetraol chloride), R_f 0.56, 3 N HCl–90% HCO_2H. Methylation with CH_2N_2 gives the diol **2**, identical to the natural product. Confirmation of this structure was obtained by formation of a non-crystalline diacetate **4** [4], M^+ 416. Relative and absolute configurations were established by comparisons of their NMR spectra and optical rotations of the Me ether **2** and Me ether diacetate **4** [4–8]. This also reveals that conversion products like the natural products **1**–**3** exist in the thermodynamically more stable *trans–cis* configuration.

The NMR spectrum of (+)-7,3′,4′-trimethoxy-2,3-*trans*-flavan-3,4-*cis*-diol **2**, mp 180° (lit. [4], mp 178.5°), $[\alpha]_D^{22}$ 52° (*c* 0.5 in MeOH), M^+ 332, R_f 0.32 ($ClCH_2CH_2Cl$–Me_2CO, 17:3) is consistent with published data [4] and in agreement with the assigned structure.

(+)-3,4,7,3′,4′-Pentamethoxy-2,3-*trans*-3,4-*cis*-flavan **3**, R_f 0.45 (C_6H_6–Me_2CO, 5:2), $C_{20}H_{24}O_6$, $[\alpha]_D^{22}$ −132° ($CHCl_3$) crystallizes in white needles, mp 287° (DMF). The NMR spectrum consists of 6 aromatic protons observed as an ABX system [τ 2.70 (*d*, *J* = 8 Hz, H-5); 3.39 (*dd*, *J* = 8 and 2 Hz, H-6); 3.54 (*d*, *J* = 2 Hz, H-8)] and an unresolved ABX system τ 2.92; 5 OMe groups τ 6.17 (*s*, 3′ + 4′-OMe); 6.24 (*s*, 7-OMe) and 6.58 (*s*, 3 + 4-OMe) and an AMX system assignable to 3 protons at positions C(2), C(3) and C(4) respectively [τ 4.92 (*d*, *J* = 10 Hz, H-2); 5.32 (*q*, *J* = 10 and 3.3 Hz, H-3) and 4.72 (*d*, *J* = 3.3 Hz, H-4)]. The structure was further deduced from the MS which gives fragments **7** and **8** as result of *retro* Diels–Alder fragmentation. The relative positions of the OMe substituents, which are favoured on biogenetic grounds were settled by conversion of **1** into **3** by exhaustive methylation with Me_2SO_4. The (2*R*,3*S*,4*S*) absolute configuration follows from comparisons of optical rotations, NMR and CD spectra of compounds **1**–**4**.



7 *m/e* 166(92.3%)



8 *m/e* 194(100%)

The singular occurrence of methoxylated flavan-3,4-diols **2** and **3** is striking considering that the only known examples of this class are the 8-*O*-methyl derivatives [4] of (2*R*,3*S*,4*S*)-flavan-3,4,7,8,3′,4′-hexaol (melacacidins) **5** and (2*R*,3*S*,4*R*)-flavan-3,4,7,8,4′-pentaol (teracacidins) **6**, including the 3-*O*-methyl ether of the former [9].

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