1582. UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 335 (3.87), 262 (4.71). EIMS, 70 eV m/z (rel. int.): 354.1455 (calc. for $C_{21}H_{22}O_5$: 354.1467; 55), 339.1189 (calc. for $C_{20}H_{19}O_5$: 339.1232; 100), 321.1164 (calc. for $C_{20}H_{17}O_4$: 321.1127; 6).

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5,7,3′-TRIHYDROXY-6,8-DI-*C*-METHYL-4′,5′-DIMETHOXYFLAVANONE FROM *ALLUAUDIOPSIS MARNIERIANA*

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Key Word Index—*Alluaudiopsis marnieriana*; Didiereaceae; 5,7,3′-trihydroxy-6,8-di-*C*-methyl-4′,5′-dimethoxyflavanone; new natural compound.

Abstract—From bark and spines of *Alluaudiopsis marnieriana*, a novel flavanone has been isolated and identified as 5,7,3′-trihydroxy-6,8-di-*C*-methyl-4′,5′-dimethoxyflavanone by UV, ^{1}H NMR and mass spectroscopy.

Previous studies of flavonoids of Didiereaceae have revealed different *C*- and *O*-methylated flavonols [1–7]. Of the four genera of this family, *Didierea*, *Decaryia*, *Alluaudia* and *Alluaudiopsis*, only the latter lacks flavonols; instead it produces flavanones. We now report the structural elucidation of a new natural compound of this class, 5,7,3′-trihydroxy-6,8-di-*C*-methyl-4′,5′-dimethoxyflavanone from *Alluaudiopsis marnieriana* Rauh, which was originally thought to be the 4′-hydroxy-3′-methoxy isomer [8].

The grey-violet fluorescence in UV light and the UV spectrum in methanol, band II main peak at 297 nm and band I at 348 nm, appeared typical of a flavanone [9]. This was confirmed by the presence of characteristic signals at δ5.34 (1H, *dd*) and at 3.04 and 2.75 (1H, *dd*) corresponding to H-2 and H-3, respectively, in the ^{1}H NMR spectrum. Moreover, this spectrum exhibited signals at δ1.97 (3H, *s*) and 1.99 (3H, *s*) and δ3.71 (3H, *s*) and 3.80 (3H, *s*) typical for two C–Me and two methoxyls, respectively, and only two aromatic proton signals at δ6.67 (1H, *d*, $J = 2$ Hz) and 6.69 (1H, *d*, $J = 2$ Hz) corresponding to two protons in the *m*-position. The positive results obtained after irradiation of each aromatic signal indicated that these protons were located in the B ring at C-2′ and C-6′. The mass spectrum exhibited a molecular ion peak at m/z 360 (85 %) in accord with a flavanone containing three hydroxyl, two methoxyl and two *C*-methyl substituents ($C_{19}H_{20}O_7$, calc. 360.1209, found 360.1213). After fragmentation, a peak at m/z 207 ($[M]^+$ B ring according to ref. [10]) and high resolution measurement of peak B at m/z 180 ($C_{10}H_{12}O_3$ calc. 180.0786, found 180.0781) indicated that the B ring was substituted by one hydroxyl and two methoxyl groups. Of the two structural possibilities, 4′-hydroxy-3′,5′-dimethoxy or 3′-hydroxy-4′5′-dimethoxy, the latter seemed more likely since in ^{1}H NMR spectrum the proton signals as well as those of methoxyl groups were separated. Nevertheless, this conclusion was confirmed by an NOE experiment; after irradiation of each methoxyl, only the irradiation on the methoxyl at δ3.80 (C-5′) gave rise to a significant result in the singlet at 6.69 (C-6′). In the A ring, two hydroxyls were located at C-5 and C-7, band II showing a bathochromic shift (43 nm) after addition of sodium methoxide in the UV spectrum [9]. The two remaining *C*-methyl groups were, thus, located at C-6 and C-8. High resolution measurements of ion fragments obtained after RDA reaction of peak D at m/z 181 ($C_9H_9O_4$ calc. 181.0501, found 181.0503) and

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peak A 180 ($C_9H_8O_4$ calc. 180.0423, found 180.0422) confirmed the A ring configuration. This new natural compound is, thus, 5,7,3′-trihydroxy-6,8-di-*C*-methyl-4′,5′-dimethoxyflavanone and not, as described in ref. [8] and cited in ref. [11], as the B ring isomer.

This is the first *C*-methylflavanone to be found in the Didiereaceae; the simultaneous presence of *O*- and *C*-methylation is typical in this family. Such *C*-methylated flavonoids are relatively rare in nature [12].

EXPERIMENTAL

Material: *Alluaudiopsis marnieriana* was collected in the South of Madagascar. 100 g of bark and spine powder was directly extracted with Et_2O. After evaporation of solvent, the dry residue was dissolved in MeOH and chromatographed on polyamide column (Macherey Nagel SC 6) with C_6H_6 progressively enriched in MeCOEt-MeOH (13). The ultimate purification of the fraction containing the new flavanone was assured by TLC on polyamide (MNDC 6) with C_6H_6-Petrol b.p. 100-140°-MeCOEt-MeOH (60-26-7-7). UV fluorescence: grey-violet; Rf ($\times 100$): TLC, polyamide MNDC 11, $CHCl_3$-MeOH-MeCOEt-$AcCH_2Ac$: 60-10-5-1, 85.UV.λ_{max} nm: MeOH: 297, 348; +NaOAc: 340; +NaOAc +H_3BO_3: 299, 341; +$AlCl_3$:319, 410; +$AlCl_3$ + HCl: 317, 352 sh, 408; +NaOH: 340 stable. MS: 70 eV, *m/z* (%): 360 (85%), 207 (15%), 181 peak D (90%), 180 (100%, peak A (50%) + peak B (50%)), 167 (40%), 152 (30%). ^1H NMR 360 MHz Bruker (C_6D_6): δ6.69 (1H, $J = 2$ Hz); 6.67 (1H, $J = 2$ Hz); 5.34 (1H, *dd*, $J = 12$ Hz, $J = 2$ Hz); 3.80 (3H, *s*); 3.71 (3H, *s*); 3.04 (1H, *dd*, $J = 15$ Hz, $J = 12$ Hz); 2.75 (1H, *dd*, $J = 15$ Hz, $J = 2$ Hz)); 1.99 (3H, *s*); 1.97 (1H, *s*).

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6-HYDROXYFLAVONES FROM *THYMBRA SPICATA*

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Key Word Index—*Thymbra spicata*; Labiatae; 6-hydroxyflavones; 6-hydroxyluteolin 7,3′-dimethyl ether; 6-hydroxyluteolin 7,3′,4′-trimethyl ether.

Abstract—Four flavonoids, including two new compounds, were isolated from the leaf extract of *Thymbra spicata*. The new compounds were the 7,3′-dimethyl and 7,3′,4′-trimethyl ethers of 6-hydroxyluteolin. All the compounds were identified by spectral methods.

INTRODUCTION

This is the first chemical investigation of *Thymbra spicata*, a member of the Labiatae. From a leaf extract four flavonoids were identified: the known compounds luteolin and rhamnetin and two new 6-hydroxyflavones, **1** and **2**.

RESULTS AND DISCUSSION

One of the new flavones, **1** was previously reported as its 6-*O*-glucoside from *Citharexylum subserratum* (Verbenaceae) [1]. The following data established the structure of **1**. A molecular ion for the flavone at M^+ 330 indicated the presence of three hydroxyl and two methoxyl groups. The presence of hydroxyl groups at C-5, C-6 and C-4′ was supported by the somewhat unusual color reactions when the compound was viewed on paper under UV light with and without ammonia. A purple color under UV light indicated a 5-hydroxyl. The dark yellow color with ammonia supported, on the one hand, a 4′-hydroxyl, but the darkness of the spot also suggested the presence of a 6-hydroxyl. Compounds with a 6-hydroxyl group usually show little or no color change with