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^{1}H NMR spectra were recorded using TMS as internal standard. Analytical and prep. TLC were performed with precoated silica gel G plates (Kieselgel 60, F-254). A Waters Associates HPLC unit equipped with a 440 absorbance and R401 refractive index detectors, employing a μ-Porasil 30 cm × 3.9 mm column was used for HPLC purifications.

Fresh *Desmarestia aculeata* (1.5 kg, wet wt), collected at Maces Bay, New Brunswick (November 1981), was finely chopped and immersed in MeOH and then extracted with MeOH in a Soxhlet for 48 hr. The extract was concd under red. pres. and the residue (30 g) dissolved in H_2O (300 ml) and extracted with $CHCl_3$ (3 × 500 ml). Evapn of the $CHCl_3$ extract yielded a brown solid (12 g) which was subjected to column chromatography on silica gel G (250 g), eluting with hexane, hexane–EtOAc, $CHCl_3$ and $CHCl_3$–MeOH in sequence. Fractions were examined by TLC, combined and purified by prep. TLC and HPLC. In order of elution, the following were obtained: β-carotene (0.07 g), plastoquinone-9 (0.01 g), *trans*-phytol (0.09 g), triglycerides (2.1 g), free sterols (0.10 g), sterol **1**, fucoxanthin (1.6 g).

Crude sterol **1** (0.037 g), a white solid, was purified by HPLC (5% MeOH in $CHCl_3$) and analysed by GC to provide pure sterol **1** (0.011 g) as granular crystals, mp 127–130°; IR ($CHCl_3$) cm^{-1}: 3500, 1450, 1320, 1150; ^{1}H NMR ($CDCl_3$): δ0.65 (*s*, 3H, 18-Me), 0.84 (*d*, 3H, J = 5 Hz, 24-Me), 0.88 (*d*, 3H, J = 5 Hz, 25-Me), 0.96 (*d*, 3H, J = 6 Hz, 21-Me), 1.00 (*s*, 3H, 19-Me), 3.51 (*m*, 1H, 3-H), 5.16 (*dd*, 1H, $J_{27A,27B}$ = 2, $J_{27A,26}$ = 11 Hz, 27-H_A), 5.28 (*dd*, 1H, $J_{27B,27A}$ = 2, $J_{27B,26}$ = 17 Hz, 27-H_B), 5.75 (*dd*, 1H, $J_{26,27A}$ = 11, $J_{26,27B}$ = 17 Hz, 26-H), 7.08 (*br s*, 1H, 30-H); MS, *m/z* (rel. int.): 400 $C_{27}H_{44}O_2$, $[M]^+$ (100), 385 $[M-Me]^+$ (22), 382 $[M-H_2O]^+$ (53), 367 $[M-H_2O-Me]^+$ (28), 357 $[M-Me_2CH]^+$ (11), 314 (42), 271 $[C_{19}H_{27}O]^+$ (14), 255 $[C_{19}H_{27}]^+$ (15), 231 $[C_{16}H_{23}O]^+$ (17), 213 $[C_{16}H_{21}]^+$ (39).

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CHAMAEJASMIN, A BIFLAVANONE FROM WOOD OF *DIPHYSA ROBINIOIDES*

OSCAR CASTRO C. and VIVIAN VALVERDE R.

Escuela de Química, Universidad de Costa Rica, Centro de Investigaciones en Química de Productos Naturales, CIPRONA, San José, Costa Rica

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Key Word Index—*Diphysa robinioides*; Leguminosae; chamaejasmin; biflavanone; fungitoxin.

Abstract—The biflavanone chamaejasmin has been isolated from the wood of *Diphysa robinioides* and its structure established by the spectral data of the biflavanone and its hexaacetyl derivative.

Diphysa robinioides Benth is the only member of this tropical genus of the Leguminosae found in Costa Rica, where it occurs widely, and is commonly known as 'Guachipelín'. This tree can reach a height of 15 m, its wood is deep yellow in colour, very hard, resistant to attack by insects and to putrefaction. For this reason it is used in the construction industry where it may be exposed to a high degree of humidity. In Guatemalian folk medicine, this plant is reported to be useful in the treatment of cancer [1].

This communication describes the isolation and structural elucidation of the dimeric flavanone 5,7,4′,5″,7″,4‴-hexahydroxy-(3,3″)-biflavanone (**1**), from the wood of *Diphysa robinioides*. This biflavanone has been isolated only once before, from *Stellara chamaejasmine* (Thymeliaceae) [2].

Compound **1** is a crystalline product of mp 225–227° (MeOH–C_6H_6). Its ^{1}H NMR spectrum ($CDCl_3$, 100 MHz) exhibits very few signals but all of them constitute well-defined coupling systems which integrate

mainly for six aromatic protons, two aliphatic protons and a characteristic phenolic proton in a region such that comparison with model compounds such as pinocembrin, naringenin and other similar compounds shows its flavanone nature.

The signals at δ6.98 (*d*, J = 8.0 Hz) and 6.93 (*d*, J = 8.0 Hz) respectively show the presence of an aromatic ring, *para*-substituted, whose protons H-2′, H-6′ and H-3′, H-5′ exhibit the characteristic *ortho*-coupling. The signals at δ6.00 (*d*, J = 3.5 Hz) and 5.91 (*d*, J = 3.5 Hz) show the presence of the aromatic protons H-6 and H-8 with the characteristic *meta* coupling. The lower field signal at 12.10 (*s*) accounts for the presence of a phenolic group at C-5 which is involved in hydrogen bonding with the C-4 carbonyl group and was further identified by IR absorption at 1620 cm^{-1}. The signals at δ5.88 (*d*, J = 12 Hz) and 2.83 (*d*, J = 12 Hz) respectively agree with the values reported in the literature for aliphatic protons H-2 and H-3 with *trans*-coupling in flavanone structures which lack oxygenated or aromatic substituents at C-3 [3, 4].

Characteristic shifts in the UV spectra were observed upon addition of sodium acetate which showed the presence of phenolic protons at C-7 and C-4′. In the same way, the bathochromic shift observed upon addition of aluminium chloride and the stability in acid media of the complex formed confirmed the existence of a phenolic group at C-5 [5]. The mass spectrum showed a molecular ion peak $[M]^+$ at m/z 542 (0.4%), consistent with a biflavanoid having six hydroxyl groups ($C_{30}H_{22}O_{10}$). A $[B]^+$ fragment at m/z 271 (8.2%) established the presence of a monomer of naringenin. From this point, the fragmentation pattern is similar to that observed in the monomer. The hexa-acetate of **1** had $[M+1]^+$ at m/z 795 (1%) and the successive loss of six acetyl groups from the molecular ion peak could be followed. The NMR spectrum confirmed the presence of six acetyl groups in compound **2**. ^{13}C NMR assignments of signals were made by analogy with the published values for naringenin and related dimers [6–8], where at least one of the monomers is naringenin, being superposable except for the C-3 signal, which in naringenin absorbs at 42.0 ppm and in our case at 49.4 ppm. This is probably due to the substitution effect of the interflavonoid linkage.

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Plant material. Diphysa robinioides Benth was collected at Canoas, Alajuela and identified by L. Poveda, botanist of The Herbarium of the National Museum of Costa Rica, San José, where a voucher has been deposited.

Extraction and isolation. Dried ground wood (2.25 kg) of *Diphysa robinioides* was exhaustively extracted with 95% EtOH by percolation at room temp. The EtOH extracts were concd to leave a semi-solid residue (450 g), which was suspended in H_2O–MeOH (4:1) and extracted several times with petrol, Et_2O and EtOAc, yielding 12.0, 184 and 78.4 g of residue, respectively. The petrol and the EtOAc extracts were set aside for further investigation. A 50 g aliquot of the Et_2O extract was chromatographed on a silica gel column using $CHCl_3$ and $CHCl_3$–MeOH mixtures of increasing polarity to eluate the column. Several fractions eluted with $CHCl_3$–MeOH (19:1) yielded, after evapn of solvent and recrystallization from C_6H_6–MeOH, 4 g **1** as a light beige, amorphous material. Chamaejasmin (**1**): UV λ_{max}^{MeOH} nm (log ε): 224 (4.60), 305 (4.36), 330 (4.23); $\lambda_{max}^{MeOH+NaOH}$ nm (log ε): 230 sh (4.50), 247 (4.47), 335 (4.67); $\lambda_{max}^{MeOH+NaOH+H_2SO_4}$ nm (log ε): 228 sh (4.54), 300 (4.45); $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε): 225 (4.67), 248 sh (4.15), 337 (4.59); $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 230 (4.66), 316 (4.57); $\lambda_{max}^{MeOH+AlCl_3+H_2SO_4}$ nm (log ε): 228 (4.93), 248 sh (4.15), 326 (4.47). ^1H NMR (100 MHz, $CDCl_3$): δ6.98 (*d*, J = 8.0 Hz, H-2′, H-6′), 6.93 (*d*, J = 8.0 Hz, H-3′, H-5′), 6.00 (*d*, J = 3.5 Hz, H-8), 5.91 (*d*, J = 3.5 Hz, H-6), 5.88 (*d*, J = 12 Hz, H-2), 2.83 (*d*, J = 12 Hz, H-3), 12.36 (*s*, OH-5). ^{13}C NMR ($CDCl_3$, 100 MHz): δ83.19 (C-2), 49.38 (C-3), 195.93 (C-4), 102.16 (C-4a), 163.50 (C-5), 96.21 (C-6), 165.63 (C-7), 94.92 (C-8), 162.36 (C-8a), 127.27 (C-1′), 128.79 (C-2′), 115.30 (C-3′), 157.34 (C-4′), 115.30 (C-5′), 128.79 (C-6′). MS m/z (rel. int.): 542 $[M]^+$ (0.4), 296 (0.8), 273 (14.2), 272 (6.3), 271 (8.2), 153 (8.4), 152 (1), 144 (2.5), 127 (32.5), 126 (13), 120 (3.8), 94 (41.6), 95 (100).

Hexa-acetate **2**: Acetylation with Ac_2O–pyridine at room temp. yielded the white amorphous hexa-acetate, mp 119–121°. ^1H NMR (100 MHz, $CDCl_3$): δ7.04 (*s*, 4H), 6.63 (*d*, J = 3.5 Hz, H-8), 6.51 (*d*, J = 3.5 Hz, H-6), 5.94 (*d*, J = 12 Hz, H-2), 2.58 (*d*, J = 12 Hz, H-3), 2.83*, 2.31*, 2.26* (*s*, 9H, MeC=O, C-4′, C-5, C-7). *Signals may be reversed. MS m/z (rel. int.): 795 $[M+1]^+$ (1), 753 (1.8), 711 (5.8), 669 (4.3), 627 (1), 543 (1.1), 397 (1), 398 (0.8), 356 (5.5), 355 (10.2), 315 (25.1), 314 (8.1), 313 (10.5), 271 (5), 237 (2.4), 195 (10.6), 162 (0.3), 153 (8.4), 135 (1.7), 120 (2.4), 107 (12.7), 62 (100).

Preliminary assays of the crude extract of this plant showed a powerful fungitoxic action. For this reason we are making an exhaustive study of all parts of the plant.

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