1145, 1005, 845. UV (EtOH) λ_{max} nm: 223, 262, 301 and 336. ^{1}H NMR 2.52 (3H, *s*), 3.91 and 3.96 (each 3H, *s*), 7.05 (2H, *s*), 7.62 (1H, *s*). MS *m/z* 220.0720 (M^+, $C_{12}H_{12}O_4$), 205.0448 ($M^+ - CH_3$), 177.0560 ($M^+ - C_2H_3O$), 149.0590 ($M^+ - C_3H_3O_2$), 135.0428 ($M^+ - C_4H_5O_2$). Found: C, 65.27; H, 5.48. Calc. $C_{12}H_{12}O_4$ requires: C, 65.45; H, 5.49.

Hydrogenation of eupatarone. 1 (70 mg) was dissolved in EtOH (20 ml) and hydrogenated for 3 hr over Pd–C (10%). This gave after chromatography (Si gel, Be) two components: **3** (20 mg) ^{1}H NMR 9.00 (3H, *t*), 1.70 (2H, *m*), 2.70 and 3.13 (each 1H, *q*, $J = 14$, 8 Hz), 3.68 and 3.74 (each 3H, *s*), 4.56 (1H, *q*), 6.26 and 6.60 (each 1H, *s*). MS *m/z* 208 (M^+), 193, 82. **2** (22 mg) ^{1}H NMR 1.16 (3H, *dd*), 3.00 (2H, *m*), 6.68 and 6.72 (each 3H, *s*), 3.90 (1H, *m*), 4.51 (1H, *m*), 6.27 (1H, *d*), 6.62 (1H, *brs*). MS *m/z* 224 (M^+), 209, 191, 179, 167, 83.

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AMORININ, A PRENYLATED CHROMENOFLAVANONE FROM *AMORPHA FRUTICOSA*

ZS. RÓZSA, J. HOHMANN, J. REISCH,* I. MESTER* and K. SZENDREI

Department of Pharmacognosy, University Medical School, Szeged, Hungary; *Department of Pharmaceutical Chemistry, Westfalia Wilhelm University, Münster, W. Germany

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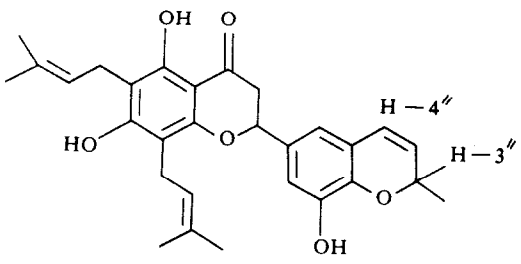
Key Word Index—*Amorpha fruticosa*; Leguminosae; amorinin; prenylated flavanone.

Abstract—A diprenylated chromenoflavanone has been characterized from the root bark of *Amorpha fruticosa*.

From the roots of *Amorpha fruticosa* L. amorphigenin, formononetin, ononin, wistin and amorphaquinone have been isolated recently by Shibata *et al.*[1]. In the course of our investigation on the constituents of the root-bark of the plant, a new prenylated chromenoflavanone (**1**) has been obtained, named amorinin. The present communication reports the structural determination of this oily component.

The presence of phenolic hydroxyl groups in **1** was indicated by the strong coloration with methanolic ferric chloride. The compound has UV absorption characteristic for flavanone derivatives[2] (λ_{max}^{MeOH} nm) log ϵ [273 sh (4.27), 285 (4.35), 300 (4.39) and 345 (4.07)].

The ^{1}H NMR spectrum (90 MHz, $CDCl_3$) shows two isopentenyl side-chains (δ 5.31, *m*, 3H, 2*x* $-CH_2-CH=$ + H-2; 3.31, *m*, 4H, 2*x* $-CH_2-CH=$; 1.73, *s*, 6H, 2*x* $-CH_3$; 1.71, *s*, 6H, 2*x* $-CH_3$) and one 2,2-dimethylchromene moiety (δ 6.32, *d*, 1H, $J = 9.9$ Hz, H-4″; 5.64, *d*, 1H, $J = 9.7$ Hz, H-3″). The singlet at δ



1

12.31 (1H) and the multiplet at δ 2.90 (2H) are characterisic for a chelated-OH and H-3, respectively [2].

The mass spectrum gave the molecular formula $C_{30}H_{34}O_6$ for amorinin (1). The RDA fragment *m/z* (rel. int.) at 288 (3) represents two hydroxyl and two prenyl groups on ring A. This fragment further stabilizes by the loss of $-C_3H_7$, $-C_4H_7$ and $-C_3H_7$–C_4H_8 at *m/z* 245 (11), 233 (21) and 189 (49) [3, 4]. The 45-nm bathochromic shift of the 300-nm band in the UV spectrum upon addition of NaOAc suggests the non-chelated hydroxyl to be at C-7 [5]; hence the prenyl groups can be located to C-6 and C-8, respectively.

The RDA fragment at *m/z* 202 (23) and the ion at *m/z* 187 (55) arising from it by the loss of a methyl group indicate that ring B has one dimethylchromene and one hydroxyl group. The *meta*-coupled doublets at δ 6.89 (1H, $J = 2.2$ Hz, H-2′) and 6.62 (1H, $J = 2.0$ Hz, H-6′) (Δ H-6′ and H-2′ 0.27 ppm) indicate the attachment of the dimethylchromene ring system at the 4′, 5′-positions and the hydroxyl group at C-3′, as in structure 1. For the isolated compound the trivial name amorinin (1) is proposed.

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APIGENIN 7-GLUCOSIDE DIACETATES IN LIGULATE FLOWERS OF *MATRICARIA CHAMOMILLA*

CLAUDIO REDAELLI, LINA FORMENTINI and ENZO SANTANIELLO*

Laboratori Ricerca Bonomelli, 22042 Dolzago (Como), Italy; *Istituto di Chimica, Facoltà di Medicina, Università di Milano, Via Saldini, 50 I-20133 Milano, Italy

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Key Word Index—*Matricaria chamomilla*; Compositae; ligulate flowers; apigenin glucosides; apigenin 7-*O*-β-glucoside diacetates; ^{13}C NMR.

Abstract—From ligulate flowers of *Matricaria chamomilla* was isolated a mixture of apigenin 7-*O*-β-glucoside diacetates, which was shown to be based on (2″, 3″)- and (3″, 4″)-diacetates.

INTRODUCTION

Apigenin (5, 7, 4′-trihydroxyflavone) and its glucosides are the main flavonoids of *Matricaria chamomilla* L. [1]. Tyihak *et al.* have already shown by PC that a few unspecified apigenin glucosides are present in the flower of the above plant [2]. Apart from the most abundant 7-*O*-β-glucoside (1), also monoacetates, mainly 6″-acetate (2), are present in the flowers [3, 4]. We now present evidence that a mixture of diacetates, 3 and 4, can be isolated from the same source.

RESULTS AND DISCUSSION

During our work of standardization of active components of *Matricaria chamomilla* L. [1, 5, 6], it happened that from ligulate flowers of some plants, collected either in particular places or times of the year, it was sometimes possible to isolate by CC a fraction of polarity similar to the monoacetate (2). This compound was apparently also homogeneous when analysed by reverse phase HPLC with the system of elution described for 1 and 2 [1]. In fact the chromatogram exhibited a single peak with a retention