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# AMORADIN, AMORADICIN AND AMORADININ, THREE PRENYLFLAVANONES FROM *AMORPHA FRUTICOSA*

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**Key Word Index**—*Amorpha fruticosa*; Leguminosae; amoradin; amoradicin; amoradinin; prenylated flavanones.

**Abstract**—Three new prenylflavanones, amoradin, amoradicin and amoradinin, were isolated from the root bark of *Amorpha fruticosa*. Their structures were deduced from chemical and spectral evidence.

## INTRODUCTION

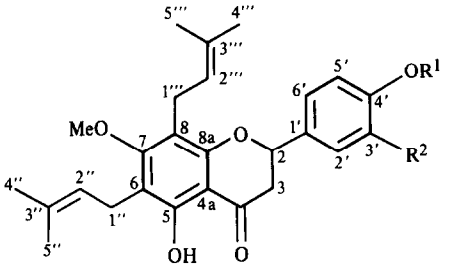
Continuing our investigations on the benzene-soluble constituents of the root bark of *Amorpha fruticosa* [1–4], we have isolated three new prenylflavanones in crystalline form: amoradin (mp 51–52°), amoradicin (mp 60–65°) and amoradinin (mp 51–54.5°). This paper reports their structures as **1**, **2** and **3**, respectively, based on spectroscopic evidence as well as chemical transformations.

## RESULTS AND DISCUSSION

Phenolic hydroxyl groups were indicated in each molecule by positive ferric chloride tests as well as strong hydroxyl IR absorption at *ca* 3350 $cm^{-1}$. Flavanone-type structures were suggested for **1–3** by UV and $^1H$ NMR data [5]. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): **1** 285 (4.40), 362 (3.81); **2** 286 (4.25); 363 (3.68); **3** 286 (4.40), 362 (3.70); $^1H$ NMR (90 MHz, $CDCl_3$): **1** $\delta$5.22 (*m*, H-2), 2.95 (*m*, H-3); **2** 5.20 (*m*, H-2), 2.95 (*m*, H-3); **3** 5.27 (*m*, H-2), 2.86 (*m*, H-3).

The $^1H$ NMR spectra of **1** and **2** showed signals for two C-linked 3,3-dimethylallyl (prenyl) side chains, a chelated hydroxyl group and a methoxyl substituent. $^1H$ NMR: **1**: $\delta$12.03 (*s*, OH), 3.75 (*s*, OMe), 5.22 (*m*, $-CH_2-\underline{CH}=$), 3.27 (*m*, $-\underline{CH_2}-CH=$), 1.78 (*s*), 1.65 (*s*), 1.61 (*s*), 1.56 (*s*, 4 × Me); **2**: 12.00 (*s*, OH), 3.75 (*s*, OMe), 5.20 (*m*, $-CH_2-\underline{CH}=$), 3.27 (*m*, $-\underline{CH_2}-CH=$), 1.77 (*s*), 1.64 (*s*, 4 × Me). The multiplet at $\delta$6.89 indicated a 3′,4′-disubstituted ring B in **2**, and the doublets at $\delta$7.30 ($J$ = 9 Hz) and 6.86 ($J$ = 9 Hz) characterized a 4′-substituted ring B in **1**.

A retro-Diels–Alder reaction of the parent ions resulted in the well-known fragmentation pattern of flavanones [5]. The $[A]^+$ fragment was identical in both compounds ($m/z$ 302) showing ring A to be substituted by a chelated




| | $R^1$ | $R^2$ |
|---|---|---|
| **1** | H | H |
| **2** | H | OH |
| **3** | H and OMe | |

Table 1. $^{13}C$ NMR spectral data of compounds **1** and **2**

| C | 1 | 2 | C | 1 | 2 | C | 1 | 2 |
|---|---|---|---|---|---|---|---|---|
| 2 | 78.42 | 78.41 | 1′ | 130.08 | 131.41 | 1″ | 21.23 | 22.32 |
| 3 | 42.47 | 43.54 | 2′ | 127.72 | 114.18 | 2″ | 122.85 | 122.76 |
| 4 | 197.58 | 197.63 | 3′ | 115.53 | 143.88 | 3″ | 131.29 | 131.66 |
| 4a | 104.42 | 105.47 | 4′ | 157.07 | 143.98 | 4″ | 17.85 | 17.83 |
| 5 | 154.42 | 158.28 | 5′ | 115.53 | 115.71 | 5″ | 24.77 | 25.67 |
| 6 | 114.15 | 113.50 | 6′ | 127.72 | 119.02 | 1‴ | 21.68 | 22.77 |
| 7 | 164.15 | 165.36 | OMe | 61.06 | 61.61 | 2‴ | 123.07 | 122.86 |
| 8 | 122.85 | 115.42 | | | | 3‴ | 131.62 | 131.86 |
| 8a | 158.40 | 159.68 | | | | 4‴ | 17.85 | 17.83 |
| | | | | | | 5‴ | 24.77 | 25.67 |

Chemical shifts in $\delta$ values from internal TMS for $CDCl_3$ solutions at 22.6 MHz.

hydroxyl, a methoxyl and two prenyl groups. According to the fragment $[B]^+$, **1** has a hydroxyl ($m/z$ 120) in the 4'-position, while **2** has two hydroxyl groups ($m/z$ 136) in the 3',4'-position.

The substitution pattern of ring A was determined by the $^{13}C$ NMR chemical shifts (Table 1), by placing the methoxyl group at C-7 and the prenyl substituents at C-6 and C-8 in **1** (5,4'-dihydroxy-7-methoxy-6,8-di-*C*-prenylflavanone) and **2** (5,3',4'-trihydroxy-7-methoxy-6,8-di-*C*-prenylflavanone).

The $^1H$ NMR spectrum of **3** showed two methoxyl groups ($\delta$3.91, 3.75) and a chelated hydroxyl group ($\delta$12.02). Methylation gave a product which was identical to the dimethyl ether of **2**. Compounds **2** and **3** had identical UV spectra with diagnostic reagents, thus one of the methoxyl groups in **3** must be at C-7. On the basis of these data it could not be decided whether the second methoxyl is at the C-3' or at the C-4'-position. The structural investigations could not be extended because of scarcity of the isolated compound.

## EXPERIMENTAL

*Extraction and isolation.* Dried, powdered root bark of *A. fruticosa* L. (14 kg) was percolated with MeOH (70 l.). The extract was evapd to 6 l., diluted with $H_2O$ (6 l.) and extracted with $C_6H_6$. Evapn of the $C_6H_6$ fraction yielded a brown, oily residue (290 g), which was fractioned on a silica gel column with petrol and petrol–$CH_2Cl_2$ (19:1, 9:1, 4:1, 7:3, 1:1), then on a polyamide column (MeOH–$H_2O$, 2:3, 3:2, 7:3, 4:1). The flavanone-containing fractions were purified on silica gel prep. layers in *n*-hexane–$Me_2CO$ (4:1), *n*-hexane–EtOAc (4:1) and $C_6H_6$–EtOAc (19:1). By this method, 10 mg of amoradin (**1**), 610 mg of amoradicin (**2**) and 1.5 mg of amoradinin (**3**) were obtained in crystalline form. $R_f$ ($C_6H_6$–EtOAc, 19:1): **1** 0.28; **2** 0.09; **3** 0.42; (*n*-hexane–$Me_2CO$, 4:1): **1** 0.22; **2** 0.10; **3** 0.23.

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# PHENOLIC DERIVATIVES FROM *ARTEMISIA CAMPESTRIS* SUBSP. *GLUTINOSA*

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**Key Word Index**—*Artemisia campestris*; Compositae; flavonoids; acetophenone derivatives.

**Abstract**—From the hexane extract of *Artemisia campestris* subsp. *glutinosa*, sakuranetin, dihydroquercetin-7,3'-dimethyl ether and three acetophenone derivatives identified as 3-[4-acetoxyisopent-2(*Z*)-enyl]-4-hydroxyacetophenone, 3-[4-acetoxyisopent-2(*E*)-enyl]-4-hydroxyacetophenone and 3-(3-acetoxymethyl-2-hydroxybut-3-enyl)-4-hydroxyacetophenone, have been isolated.

## INTRODUCTION

Column chromatography of the weakly acidic fraction of the hexane extract of *Artemisia campestris* L., subsp. *glutinosa* (Gay ex Besser) Batt., afforded the previously reported acetophenone derivatives [1, 2], sakuranetin [3], dihydroquercetin-7,3'-dimethyl ether [4] and three acetophenone derivatives, **1–3**.

## RESULTS AND DISCUSSION

Compounds **1** and **2** were chromatographically very similar and showed practically the same spectral properties: $[M]^+$ at $m/z$ 262 ($C_{15}H_{18}O_4$); IR spectra with bands at $\nu_{max}$ 3300 (OH), 1680 (C=O), 1640 (C=C), 1600, 1500 (aromatic) and 1740, 1270 (OAc) $cm^{-1}$; the $^1H$ NMR spectra showed the presence of one 1,3,4-trisubstituted aromatic ring, the substituents being identified as COMe, OH and 4-acetoxyisopent-2-enyl groups (Table 1). The only significant difference was the signal due to the $CH_2OAc$ groups, which appeared in both as singlets, but at $\delta$ 4.72 in **1**, and 4.45 in **2**. This difference suggested that **1** and **2** may be one pair of (*Z*) and (*E*) stereoisomers [2]. The stereochemistry (*Z*) for **1** and (*E*) for **2**, was confirmed by acetylation and saponification of **1** and **2**, which gave **1a** or **2a** and **1b** or **2b**, respectively. Compounds **1b** and **2b** were identical in all respects with those already isolated from *A. campestris* [2].