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# PHENOLIC DERIVATIVES FROM *ARTEMISIA GLUTINOSA**

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**Key Word Index**—*Artemisia glutinosa*; Compositae; coumarin-flavonoids and acetophenone derivatives.

**Abstract**—Investigation of the aerial parts of *Artemisia glutinosa* afforded herniarin, the flavonoids naringenin, dihydroquercetin-7,3′-dimethylether, 5,3′,4′-trihydroxy-7-methoxyflavanone, palmatin, rhamnetin and three acetophenone derivatives: 2,4-diacetylanisole, dehydroespeletone and the new compound glutinosol.

## INTRODUCTION

In the course of our research on Compositae metabolites, we studied the composition of *Artemisia glutinosa*. Herniarin and several flavonoids were isolated from this plant. The aerial parts also contained three acetophenone derivatives, one of which is new and has been named glutinosol (**1**).

## RESULTS AND DISCUSSION

Column chromatography of the alcoholic extract of *A. glutinosa* Gay ex Besser [1] afforded herniarin, the flavonoid compounds naringenin, dihydroquercetin-7,3′-dimethylether, 5,3′,4′-trihydroxy-7-methoxyflavanone, palmatin (3,5,3′,4′-tetrahydroxy-7-methoxyflavanone) and rhamnetin, together with three acetophenone derivatives: 2,4-diacetylanisole [2], dehydroespeletone [3] and the new compound glutinosol (**1**).

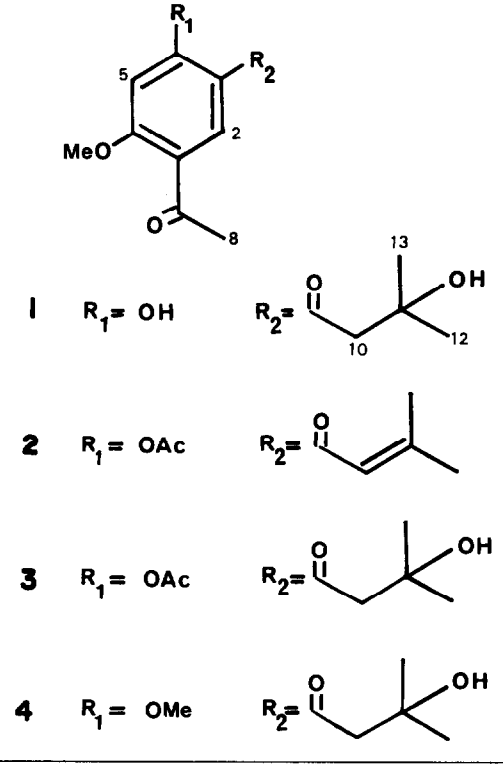


Table 1. $^1$H NMR data of compounds **1** and **4**

| | **1** | **4** |
|---|---|---|
| H-2 | 8.30 *s* | 8.26 *s* |
| H-5 | 6.48 *s* | 6.46 *s* |
| H-8 | 2.61 *s* | 2.53 *s* |
| H-10 | 3.13 *s* | 3.08 *s* |
| H-12 | 1.30 *s* | 1.28 *s* |
| H-13 | | |
| Ph-OH | 12.85 *s* | — |
| Ph-OMe | 3.96 *s* | 3.98 (6H, *s*) |

Compound **1** was isolated as a solid, mp 119°, having the molecular formula $C_{14}H_{18}O_5$, MS ($M^+$ *m/z* 266). It took on a reddish colouration with ferric chloride and exhibited UV absorption bands at $\lambda_{max}$ 252, 279 and 320 nm and IR bands at $\nu_{max}$ 3500 (OH), 1660, 1640 (CO) and 1450 (Ph-OMe) $cm^{-1}$. This functionality was confirmed by the $^1$H NMR spectrum, indicative of a tetrasubstituted aromatic ring (Table 1). A hydroxyl group was situated at C-4, because it presents difficulty, as occurred with the demethylated dehydroespeletone, in forming the acetylated derivative with acetic anhydride–pyridine. However, when the same compound was treated with acetic anhydride–sodium acetate [4], two monoacetates, **2** and **3**, were formed, the latter with mp 78°. Methylation of **1** with dimethyl sulphate gave **4**, mp 130°; IR $\nu_{max}$ $cm^{-1}$: 3400, 1650, 1600 and 1450. Its $^1$H NMR spectrum (Table 1) showed a signal due to the methoxyl group at $\delta$ 3.98.

## EXPERIMENTAL

Mps are uncorr. UV were recorded in EtOH. $^1$H NMR spectra were recorded at 90 MHz using TMS as int. standard. Analytical TLC was performed on Si gel G (Merck) and CC on Si gel 0.2–0.5 mesh.

The aerial parts of the plant (15 kg) collected in Ontígola (Toledo, Spain) were finely ground and extracted with hot EtOH. The resulting extract was separated by CC and eluted with

*Part 45 in the series "Constituents of the Compositae". For Part 44, see González, A. G., de la Rosa, A. D. and Massanet, G. M. (1982) *Phytochemistry* **21**, 895.

petrol–EtOAc mixtures and EtOAc, giving: herniarin (50 mg), naringenin (30 mg), dihydroquercetin-7,3′-dimethylether (63 mg), palmatin (210 mg), 5,3′-4′-trihydroxy-7-methoxyflavanone (50 mg), rhamnetin (90 mg), 2,4-diacetylanisole (195 mg), dehydroespeletone (600 mg) and glutinosol (155 mg).

*2,4-Diacetylanisole.* Mp 85° (EtOAc–hexane), UV $\lambda_{max}$ nm: 273 (ε 10.000), 268 (ε 6.456), 310 (ε 1.349). IR $\nu_{max}^{CHCl_3}$ cm$^{-1}$: 1670 (C=O), 1600 (aromatic); $^1$H NMR (Table 1); MS *m/z* (%) 192: [M]$^+$ (23), 177 [M − Me]$^+$ (100), 119 (44) and 91 (80).

*Glutinosol* (**1**). Mp 119°; UV $\lambda_{max}$ nm: 252 (ε 27.542), 279 (ε 10.715), 320 (ε 4.570); IR $\nu_{max}^{CHCl_3}$ cm$^{-1}$: 3500 (OH), 1660, 1640 (C=O), 1450 (Ph-OMe), 1360 (Ph-COMe); $^1$H NMR (Table 1); MS *m/z* (%): 266 [M]$^+$ (5), 251 [M − Me]$^+$ (5), 248 [M − $H_2O$]$^+$ (2), 208 [M − $C_3H_6O$]$^+$ (10), 193 [M − $C_4H_9O$]$^+$ (100), 175 (37), 135 (9). Acetylation of 35 mg ($Ac_2O$–pyridine, 2 hr, 60°) yielded the starting product. With $Ac_2O$–NaOAc, 12 hr at 70°, two acetates were obtained, one being oily (21.3 mg) **2**; IR $\nu_{max}^{CHCl_3}$ cm$^{-1}$: 1770 (ester), 1685, 1610 (C=C), 1600 (aromatic); $^1$H NMR ($CDCl_3$): δ 2.33 (3H, *s*); MS *m/z* (%): 290 [M]$^+$ (16), 248 (31), 247 (42), 233 (73), 231 (38), 230 (40), 215 (70), 205 (100), 193 (87), 175 (49). The other acetate was crystalline, **3** (15 mg), mp 78–80° ($Et_2O$–hexane); IR $\nu_{max}^{CHCl_3}$ cm$^{-1}$: 3550 (OH), 1770 (ester), 1680, 1600, 1460, 1360 and 1160; $^1$H NMR ($CDCl_3$): δ 2.35 (3H, *s*); MS *m/z* (%): 308 [M]$^+$ (1), 266 (3), 251 (5), 247 (11), 248 (12), 233 (13), 208 (11), 205 (29), 193 (100), 175 (22), 149 (29), 91 (27).

Treatment of **1** (90 mg) with dry $Me_2CO$ (5 ml), dry $K_2CO_3$ (0.5 g) and $Me_2SO_4$ (0.2 ml) with heating for 5 hr gave the Me ether, **4** (71 mg), mp 130–132° (EtOAc–hexane); IR $\nu_{max}^{CHCl_3}$ cm$^{-1}$: 3400 (OH), 1650 (C=O), 1600 (aromatic), 1450 (–OMe); $^1$H NMR (Table 1); [M]$^+$ 280 ($C_{15}H_{20}O_5$).

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# DIBENZYLBUTYROLACTONE LIGNANS FROM *VIROLA SEBIFERA**

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**Key Word Index**—*Virola sebifera*; Myristicaceae; seeds, pericarp; dibenzylbutyrolactone lignans.

**Abstract**—The fruits of *Virola sebifera* contain in the seed (2*R*, 3*S*)-3-(3,4-dimethoxybenzyl)-2-(3,4-methylenedioxybenzyl)-butyrolactone, and in the pericarp (2*R*, 3*R*)-3-(3,4-dimethoxybenzyl)-2-(3,4-methylenedioxybenzyl)-butyrolactone, (2*R*, 3*R*)-2,3-di-(3, 4-dimethoxybenzyl)-butyrolactone and (2*R*, 3*R*)-2,3-di-(3,4-methylenedioxybenzyl)-butyrolactone.

The seeds of *Virola sebifera* Aubl. were found to contain, besides the previously reported 1,11-diarylundecan-1-one and 4-aryltetralone neolignans [2], the *cis*-dibenzylbutyrolactone lignan, **1**. In the pericarp, however, two equally novel *trans*-dibenzylbutyrolactone lignans (**2a**, **2b**) were found to accompany (−)-hinokinine (**2c**).

The IR carbonyl absorptions ($\nu_{max}$ 1773 ± 6 cm$^{-1}$) of all four isolates suggested the presence of a butyrolactone system. Indeed, as $^{13}$C NMR evidence (Table 1) suggests by comparison with the known derivative **2c** [3], all compounds must be 2,3-dibenzylbutyrolactones. The nature of the substituents at C-2 and C-3 can be determined by mass spectrometry [4] (Table 2). According to Corrie *et al.* [5], relative configurations in 2,3-dibenzylbutyrolactones are given by NMR comparison of the methylene protons at C-4. Equivalence of these protons corresponds to the *cis*-configuration, while non-equivalence corresponds to the *trans*-configuration. In this respect, **1** as well as the model compound **3** [5, 6], must be *cis*-oriented, while **2a**–**2c** as well as the model compound **2d** [4] must be *trans*-oriented (Table 3). Finally, the opposite ORD curves for the *cis*-derivative **1** ($[\phi]^{pk}_{276} - 500$, $[\phi]^{tr}_{300} - 2700$), and the model compound **3** ($[\phi]^{tr}_{272} + 2300$, $[\phi]^{pk}_{295} + 4500$) [6] establish the absolute configuration of the former. The ORD curves of the *trans*-derivatives **2a** and **2b** are comparable with the curves of the model compounds **2c** and **2d** [6].

*Part XIX in the series "The Chemistry of Brazilian Myristicaceae". For Part XVIII see ref. [1]. Taken from part of the doctorate thesis presented by L. M. X. L. to the Universidade de São Paulo (1982).