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TWO NEW ACETOPHENONES FROM FRUITS
OF *EVODIA MERRILLII*

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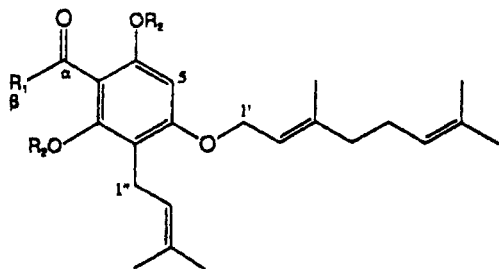
ABSTRACT.—Two new acetophenones, 4-(1'-geranyloxy)-2,6,β-trihydroxy-3-dimethylallylacetophenone [**1**], and 2-(1'-geranyloxy)-4,6,β-trihydroxyacetophenone [**2**], were isolated from the fruits of *Evodia merrillii*, and their structures were determined on the basis of spectral data.

In a previous paper (1), we have reported four acetophenones isolated from the fruits of *Evodia merrillii* Kanehira & Sasaki ex Kanehira (Rutaceae). Now we wish to report the structural elucidation of two additional acetophenones, 4-(1'-geranyloxy)-2,6,β-trihydroxy-3-dimethylallylacetophenone [**1**] and 2-(1'-geranyloxy)-4,6,β-trihydroxyacetophenone [**2**].

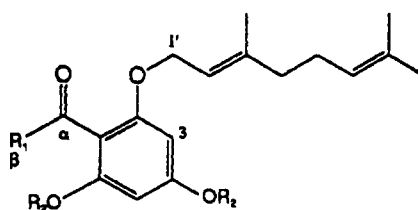
The ir spectra of acetophenones **1** and **2** suggested that aromatic rings, free OH groups, and H-bonded OH groups were present.

Compound **1** was obtained as a light yellow crystalline solid from EtOAc, mp 136–137°. Its uv spectrum in MeOH gave a phloroglucinol, type chromophore

(**2**) at λ max 291 nm (log ε 4.36). The ¹H-nmr spectrum showed the presence of an *O*-geranyl group, a dimethylallyl group, and an unsubstituted aromatic proton very similar to signals described previously for 4-(1'-geranyloxy)-2,6-dihydroxy-3-isopentenylacetophenone [**3**] (1), except for the presence of a two-proton singlet at δ 4.78 ppm and the lack of the singlet of three protons at δ 2.64 ppm. In the triacetate of **1**, the singlet of H-β appeared at δ 4.94. The downfield shift (0.16 ppm) showed that H-β was attached to an OH group. The shift of 0.16 ppm to lower field for the oxygenated -CH₂- group upon acetylation is somewhat smaller than usual. However, the 2D nmr data strongly support the



1 R₁=CH₂OH, R₂=H
3 R₁=Me, R₂=H



2 R₁=CH₂OH, R₂=H
4 R₁=Me, R₂=H

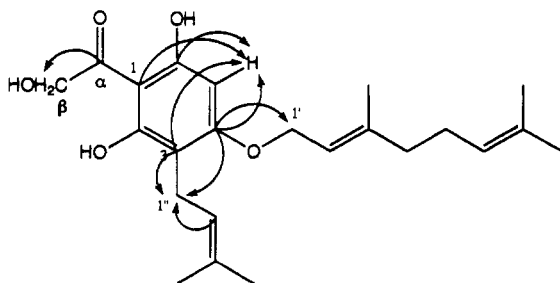


FIGURE 1. COLOC results of compound **1** in CDCl_3 ($J_{\text{CH}}=8$ Hz).

structure of compound **1** (Figure 1). The ^{13}C -nmr spectrum of **1** was also similar to that of **3** and further demonstrated the oxygenated methylene carbon at δ 68.53 (τ , C- β) instead of the acetyl group. Furthermore, the downfield shift (0.54 ppm) of H-5 of **1** triacetate compared to that of **1** supported two other OH groups at the 2,6 positions. From the above-mentioned evidence, the structure of **1**, 4-(1'-geranyloxy)-2,6, β -trihydroxy-3-dimethylallylacetophenone, was assigned.

Compound **2** was obtained as colorless needles from EtOAc/*n*-hexane. The ^1H nmr of **2** showed one geranyl group, one oxygenated methylene group, two aromatic protons, and three OH groups. The ^1H -nmr spectral data are closely similar to those of 2-(1'-geranyloxy)-4,6-dihydroxyacetophenone [**4**] (1), except that the acetyl group of **4** was replaced by an oxygenated methylene group at δ 4.71 as in **1**. The similarity of their ^{13}C -nmr spectra is depicted in Table 1. Acetylation of **2** with Ac_2O /pyridine gave the triacetate, giving further evidence for three OH groups. Considering all these observations, it was clear that compound **2** is 2-(1'-geranyloxy)-4,6, β -trihydroxyacetophenone.

EXPERIMENTAL

GENERAL METHODS AND PLANT MATERIAL.—

These are the same as previously described (1).

EXTRACTION AND ISOLATION.—The dried fruit (3.8 kg) was extracted with 95% EtOH (7 liters \times 4). The EtOH extract was concentrated under reduced pressure. H_2O (1 liter) was added to the concentrated EtOH extract, which was then

partitioned successively with Et_2O (1 liter \times 3) and *n*-BuOH (1 liter \times 3). The Et_2O layer (500 g) was further subjected successively to chromatography on Si gel (1500 g) with a gradient of *n*-hexane, EtOAc, and MeOH as eluents. In all, eighteen fractions were collected. Fractions 14–16 showed three main spots on tlc analysis. These fractions (23 g) were combined and further chromatographed on Si gel repetitively with Me_2CO - CHCl_3 (20:80) to yield **1** (1.41 g) and **2** (89.9 mg).

4-(1'-Geranyloxy)-2,6, β -trihydroxy-3-dimethylallylacetophenone [1].—Light yellow crystals from EtOAc: mp 136–137 $^\circ$; eims m/z [$\text{M}]^+$ 388 (3.6%), [$\text{M}-\text{C}_{10}\text{H}_{16}\text{J}^-$ 252 (8.6), 219 (38.6), [$\text{M}-\text{C}_{10}\text{H}_{16}-\text{C}_2\text{H}_4\text{J}^-$ 197 (6.4), 179 (15.6), 165 (37.1), 69 (100.0); hrms m/z 388.2252 (calcd 388.2249 for $\text{C}_{23}\text{H}_{32}\text{O}_5$); ir (KBr) 3450, 3120, 1635, 1595, 1520, 1260, 1085, 955 cm^{-1} ; uv max (MeOH) 291 nm ($\log \epsilon$ 4.36); ^1H nmr (CDCl_3) δ 1.59 (3H, s, Me-8'), 1.66 (3H, s, Me-9'), 1.70 (3H, s, Me-10'), 1.73 (3H, s, Me-5''), 1.79 (3H, s, Me-4''), 2.08 (4H, m, H_2 -4', H_2 -5'), 3.30 (2H, d, $J=7.0$ Hz, H_2 -1''), 3.99 (-OH), 4.53 (2H, d, $J=6.4$ Hz, H_2 -1'), 4.78 (2H, s, H- β), 5.07 (1H, m, H-6'), 5.15 (1H, t, $J=7.0$ Hz, H-2''), 5.42 (1H, t, $J=6.4$ Hz, H-2'), 6.01 (1H, s, H-5), 8.80 (-OH), 11.03 (-OH); ^{13}C nmr (CDCl_3) see Table 1.

Acetylation of **1** was performed with Ac_2O /pyridine at room temperature for 16 h and gave 4-(1'-geranyloxy)-2,6, β -triacetoxy-3-dimethylallylacetophenone, an oil: ir (neat) 1775, 1750, 1610, 1420, 1370, 1220, 1180, 1065 cm^{-1} ; ^1H nmr (CDCl_3) δ 2.12, 2.25, 2.28 (each 3H, s, OAc \times 3), 4.94 (2H, s, H_2 - β), 6.55 (1H, s, H-5).

2-(1'-Geranyloxy)-4,6, β -trihydroxyacetophenone [2].—Colorless needles from EtOAc/*n*-hexane: mp 144.5–146 $^\circ$; fabms (neg.) [$\text{M}-\text{H}]^-$ 319(100.0%), [$\text{M}-\text{C}_{10}\text{H}_{16}-\text{H}]^-$ 183(81.2); hrms m/z 320.1623 (calcd 320.1623 for $\text{C}_{18}\text{H}_{24}\text{O}_5$); ir (KBr) 3450, 3200, 1635, 1595, 1495, 1455, 1275, 1235, 1158, 1085, 825 cm^{-1} ; uv max (MeOH) 291 nm ($\log \epsilon=4.08$); ^1H nmr (CDCl_3) δ 1.59 (3H, s, Me-8'), 1.67 (3H, s, Me-9'), 1.72 (3H, s, Me-10'), 2.10 (4H, m, H_2 -4', H_2 -5'), 3.89 (-OH), 4.56 (2H, d, $J=6.6$ Hz, H_2 -1'), 4.71 (2H,

TABLE 1. ^{13}C -nmr (CDCl_3) Assignments of 1-4.^a

Carbon	Compound			
	1	3	2	4
C- α	201.78 (s)	203.51 (s)	201.72 (s)	203.50 (s)
C- β	68.53 (t)	32.81 (q)	68.57 (t)	32.99 (q)
C-1	102.67 (s)	105.29 (s)	103.71 (s)	106.35 (s)
C-2	159.94 (s)	159.67 (s)	163.38 (s)	162.73 (s)
C-3	107.08 (s)	106.52 (s)	91.76 (d)	91.60 (d)
C-4	163.66 (s)	163.01 (s)	163.92 (s)	163.11 (s)
C-5	92.83 (d)	92.77 (d)	96.55 (d)	96.29 (d)
C-6	162.79 (s)	162.52 (s)	166.95 (s)	167.17 (s)
Geranyl				
C-1'	65.60 (t)	65.41 (t)	65.95 (t)	65.74 (t)
C-2'	118.73 (d)	118.90 (d)	117.85 (d)	118.41 (d)
C-3'	141.82 (s)	141.51 (s)	142.99 (s)	142.22 (s)
C-4'	39.45 (t)	39.45 (t)	39.47 (t)	39.41 (t)
C-5'	26.29 (t)	26.28 (t)	26.27 (t)	26.21 (t)
C-6'	123.66 (d)	123.68 (d)	123.50 (d)	123.56 (d)
C-7'	131.88 (s)	131.85 (s)	132.07 (s)	131.97 (s)
C-8'	17.65 (q)	17.66 (q)	17.69 (q)	17.68 (q)
C-9'	25.57 (q)	25.59 (q)	25.61 (q)	25.62 (q)
C-10'	16.67 (q)	16.65 (q)	16.64 (q)	16.59 (q)
Dimethylallyl				
C-1''	21.53 (t)	21.59 (t)		
C-2''	121.69 (d)	121.90 (d)		
C-3''	135.01 (s)	134.94 (s)		
C-4''	17.83 (q)	17.81 (q)		
C-5''	25.78 (q)	25.80 (q)		

^aAssignments were made by the DEPT method.

d, $J=4.8$ Hz, $\text{H}_2\text{-}\beta$), 5.07 (1H, m, H-6'), 5.48 (1H, t, $J=6.6$ Hz, H-2'), 5.90 (1H, d, $J=2.2$ Hz, H-3), 6.00 (1H, d, $J=2.2$ Hz, H-5), 6.27 (brs -OH), 13.09 (brs -OH); ^{13}C nmr (CDCl_3) see Table 1.

Acetylation of **2** by the same manner yielded a triacetate, 2-(1'-geranyloxy)-4,6, β -triacetoxyacetophenone, with ir (neat) 1775, 1750, 1610, 1430, 1370, 1190, 1130, 1075 cm^{-1} ; ^1H nmr (CDCl_3) δ 2.12, 2.23, 2.26 (each 3H, s, OAc \times 3), 5.01 (2H, s, $\text{H}_2\text{-}\beta$), 6.55 (1H, d, $J=1.8$ Hz, H-3), 6.61 (1H, d, $J=1.8$ Hz, H-5).

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