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SHORT REPORTS

SESQUITERPENES FROM *CELASTRUS PRINGLEI*

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Key Word Index—*Celastrus pringlei*; Celastraceae; sesquiterpenes; β-dihydroagarofurane; pringleine.

Abstract—Three new sesquiterpene polyol esters with a β-dihydroagarofurane skeleton were isolated from *Celastrus pringlei*. Their structures were elucidated by spectroscopic means.

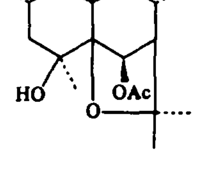
INTRODUCTION

Many sesquiterpene polyesters with a dihydro β-agarofurane skeleton have been isolated from plants of the Celastraceae family [1]. Some of them present interesting biological activity [1, 2]. In a continuation of our studies on Mexican Celastraceae species [3–5], we describe here the isolation and structural elucidation of three new derivatives of deoxymaytol which we named pringleine (**1a**), acetyl pringleine (**1b**) and 8α-benzoyloxy-acetyl-pringleine (**1c**).

RESULTS AND DISCUSSION

The methanolic extract of the stems of *Celastrus pringlei*, Rose, afforded, after extensive purification, pringleine (**1a**), acetyl pringleine (**1b**), and 8α-benzoyloxy-acetyl-pringleine (**1c**). Pringleine (**1a**) was obtained as an amorphous powder and had a molecular formula $C_{33}H_{38}O_{11}$. Its IR spectrum showed hydroxyl absorption at 3500 cm^{-1} and ester carbonyl bands at 1735 and 1720 cm^{-1}. The ^1H NMR spectrum (Table 1), revealed the presence of two acetate groups (δ2.1 and 2.25, *s*, 3H each) and two benzoate groups (δ7.25–8.15, *m*, 10H). The location of the ester group and the stereochemistry were deduced from the analysis of the ^1H NMR spin–spin coupling patterns with the aid of double resonance experiments. Thus the chemical shifts and coupling constants of H-6 (δ 6.05, *br s*) and H-7 (δ 2.45, *dd*, $J_{7\alpha,8\beta} = 4$ and $J_{7\alpha,8\alpha} = 7$ Hz) indicated the presence of an acetate group at C-6 with the usual [1, 2] β-equatorial orientation. A double doublet observed at δ5.6 was assigned to H-9, the coupling constants ($J = 1$ and 7 Hz) are appropriate for equatorial–equatorial and equatorial–axial interactions and hence the benzoate at C-9 must be β-axially oriented. The second acetate group must be attached to C-15 by comparison with related products [1, 2], the C-15 methylene is responsible for an AB system observed at δ4.45 and 5.1 ($J = 12$ Hz). A doublet at δ4.65 ($J = 4$ Hz) was ascribed to the geminal proton of a secondary hydroxyl group as it was sharpened on addition of D_2O. The secondary hydroxyl group must be bound to C-1 and the second benzoate ester at C-2, since H-2 (δ5.38 *q*) was shown to be coupled to H-1. The coupling constant ($J = 4$ Hz) exhibited by H-2 indicated equatorial–equatorial and equatorial–axial interactions of this proton with H-1, H-3 and H-3′ and hence the benzoate group at C-2 must be axially oriented as shown in **1a**.

The ^1H NMR spectrum of **1a** (Table 1) showed the three methyl groups as a singlet (9H) at δ1.45, indicating that C-4 must be totally substituted. Acetylation of **1a** gave the acetyl derivative **1b** which had hydroxyl absorption in the IR spectrum (3500 cm^{-1}), thus showing the presence of a tertiary hydroxyl group at C-4. Acetyl pringleine (**1b**) was an amorphous powder which showed molecular formula $C_{35}H_{40}O_{12}$. The doublet ascribed to H-1 was shifted downfield and appeared at δ5.67 (*d*, $J = 4$ Hz). The new acetate group was observed at δ1.56, thus proving the presence of a β-axially oriented benzoate group at C-9 in pringleine (**1a**) as it has been observed that the unusual diamagnetic shift of the acetate methyl signal is possible when an equatorial acetate at C-1 is shielded by



Ia R = R¹ = H
Ib R = Ac, R¹ = H
Ic R = Ac, R¹ = OCOPh

Table 1. ^{1}H NMR spectra of compounds **1a**, **1b** and **1c**

	1a ($CDCl_3$)	**1a** ($CDCl_3$–C_6D_6)	**1b** ($CDCl_3$)	**1b** ($CDCl_3$–C_6D_6)	**1c**($CDCl_3$)
H_1	4.72 *d* (4)	4.65 *d* (4)	5.67 *d* (4)	5.92 *d* (4)	5.82 *d* (4)
H_2	5.5 *m*	5.38 *br q* (4)	5.48 *br q* (4)	6.07 *br q* (4)	5.9 *m*
H_6	6.05 *br s*	6.05 *br s*	6.15 *br s*	6.2 *br s*	6.8 *br s*
H_7	2.55 *dd* (4, 7)	2.45 *dd* (4, 7)	2.55 *dd*	2.48 *dd*	2.55 *d* (4)
H_8	—	—	—	—	5.65 *d* (4)
H_9	5.5 *m*	5.6 *dd* (1, 7)	5.73 *br d* (7)	5.75 *dd* (1, 7)	5.80 *s*
$3H_{12}$	*1.55 *s*	1.45 *br s*	1.54 *br s*	*1.38 *s*	*1.55 *s*
$3H_{13}$	*1.58 *br s*	1.45 *br s*	1.54 *s*	*1.42 *s*	*1.68 *s*
$3H_{14}$	*1.58 *br s*	1.45 *br s*	1.54 *s*	*1.42 *s*	*1.8 *s*
$2H_{15}$	4.55, 5.1 AB*q* (12)	4.45, 5.15 AB*q* (12)	4.42, 5.27 AB*q* (14)	4.55, 5.62 AB*q* (14)	4.62–5.55 AB*q* (14)
C_1–COMe	—	—	1.56 *s*	1.57 *s*	*1.6 *s*
C_6COMe	2.1 s	1.87	2.1 s	1.75 s	2.05 *s*
C_{15}–COMe	2.25 *s*	2.05	2.25 *s*	2.0 *s*	2.15 *s*
aromatic protons	7.25–8.15 2 *m*, 10 H	7.1–8.25 2 *m*, 10 H	7.25–8.25 2 *m*, 10 H	7–8.45 2 *m*, 10 H	7.35–8.3 2 *m*, 15 H

Values in parentheses are coupling constants in Hz (TMS as internal reference 80 MHz).
*Values in any vertical column may be interchanged.

an aromatic ester axially bound to C-9 [6] in a β-dihydroagarofuran skeleton. Therefore, pringleine is the 2,9-dibenzoyl-6,15-diacetyl-deoxymaytol. The sesquiterpene ester of medium polarity was identified as the acetyl pringleine (**1b**).

The polyester of minor polarity (**1c**) showed similar spectroscopic characteristics to those of **1a** and **1b**, except for the presence in the ^{1}H NMR spectrum (Table 1) of 15 aromatic protons at δ7.35–8.3, and the multiplicity shown by H-7 (δ2.55, *d*, $J = 4$ Hz). Likewise, the mass spectrum indicates the presence of three benzoyloxy moieties [m/z 754, $[M-18]^+$, 633, 518, 390, 105 (100%)]. These data suggested the structure **1c** for this compound. The stereochemistry of the C-8 substituent was assigned considering the H-8/H-7 equatorial–equatorial interactions, the dihedral angle H-8/H-9 ($\sim$ 85°) and the multiplicity of H-9 (δ5.8, *s*), which indicate that the benzoyloxy moiety at C-8 is α-axially oriented.

EXPERIMENTAL

Mps are uncorr. MS were obtained by chemical ionization. ^{1}H NMR spectra were performed at 80 MHz with TMS as int. standard. Plant material was collected in Tepoztlán (Morelos, México) and the voucher specimen (MEXU 258575) was deposited at the herbarium of the Instituto de Biología, UNAM.

Isolation. The dried stems of *Celastrus pringlei*, Rose, (15 kg) were powdered and extracted twice with MeOH (2 x 20 l), for 5 days. The solvent was removed under red. press. to 1 l; diluted with H_2O and extracted into AcOEt (3 x 2 l). The solvent was dried and removed under red. press. and the residue (65 g) was chromatographed over silica gel (1 kg). Elution with hexane–AcOEt (9 : 1) gave 100 mg of a mixture of products which after several TLC separations afforded **1a**, **1b** and **1c**.

Pringleine (**1a**). Mp 128° (amorphous powder). IR ν_{max} cm^{-1}: 3525, 3430, 1735, 1720, 1605, 1585. ^{1}H NMR (see Table 1) MS (CI) m/z: 610 $[M]^+$, 592, 532, 472, 471, 350, 105 (100%).

Acetylpringleine (**1b**). Mp 118° (amorphous powder). IR ν_{max} cm^{-1}: 3565, 1740, 1730, 1600, 1585. ^{1}H NMR (see Table 1) MS (CI) m/z: 634 $[M-18]^+$, 592, 574, 532, 514, 471, 350, 229, 105 (100%).

8α-benzoyl-oxy-acetylpringleine (**1c**). Mp 98° (amorphous powder). IR ν_{max} cm^{-1}: 3550, 1730 (broad), 1600, 1580. ^{1}H NMR (see Table 1), MS (CI) m/z: 754 $[M-18]^+$, 633, 592, 574, 532, 512, 471, 390, 350, 229, 105 (100%).

Acetylation of **1a**. Pringleine (**1a**) (7 mg) was treated with Ac_2O–Py during 36 hr at room temp. After the usual work-up, **1b** was obtained. Comparison of this substance with the natural product, acetylpringleine, showed it to be the same compound.

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