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HOPENOL-B, A TRITERPENE ALCOHOL FROM *EUPHORBIA SUPINA*

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Key Word Index—*Euphorbia supina*; Euphorbiaceae; triterpenes; motiol; hopenol-b.

Abstract—In addition to the known triterpene motiol, hopenol-b (hop-22(29)-en-3β-ol) was isolated from the whole herb of *Euphorbia supina*. It has not been found previously in nature, though it has been prepared by both synthetic and biosynthetic methods.

INTRODUCTION

Euphorbia supina Rafin. has been reported to contain octacosanol, sitosterol and an unidentified triterpene alcohol [1]. Recent investigation on the neutral benzene extract of this plant demonstrated the presence of fern-8-en-3β-ol and supinenolone-C (3β-hydroxyfern-8-en-7,11-dione) [2].

In this paper, the isolation of motiol and a new triterpene alcohol is described.

RESULTS AND DISCUSSION

Continuous CC of the neutral benzene extract of the air-dried whole herb afforded, after the elution of fern-8-en-3β-ol, a solid mixture which could not be separated by TLC. Crystallization of the solid from ethanol gave motiol, mp 222–224°, $[\alpha]_D^{21}$ $-39.6°$ [3].

Concentration of the mother solution yielded the second triterpene alcohol (**1**), mp 251–253°, $[\alpha]_D^{21}$ $+157.8°$, M^+ at m/z 426 ($C_{30}H_{50}O$), IRν_{max}cm^{-1}: 3610, 1080 (OH) and 1638, 892 (terminal methylene). The ^1H NMR spectrum of **1** showed six tertiary methyls at δ 0.72–0.98, one isopropenyl at 1.75 (3H, *s*) and 4.78 (2H, *br s*) and one C-3 proton at 3.19 (1H, *q*).

The mass spectrum of **1** exhibited intense peaks due to the cleavage of ring C at m/z 207 and 189 along with peaks at m/z 383 and 370, indicative of the hopane or moretane skeleton [4–6]. Moreover, in contrast with the ^1H NMR spectrum of moretenol isolated by the method described in the literature [7], the C-28 methyl signal of **1** appeared at δ 0.73, which was 0.04 ppm lower than the corresponding signal of the former compound [6, 8–10]. This strongly suggested the structure of **1** to be hopenol-b [hop-22(29)-en-3β-ol].

Acetylation of **1** furnished an acetate (**2**), mp 233–235°, $C_{32}H_{52}O_2$ (M^+ at m/z 468). The ^1H NMR signal of the C-3 proton quartet in **1** shifted to δ 4.52 in the spectrum of **2**, indicating an equatorial hydroxyl group in **1**. Oxidation of **1** gave a ketone (**3**), mp 220–222°, $C_{30}H_{48}O$ (M^+ at m/z 424), identical with hopenone-b which is known in nature [11].

Finally, the structure of **1** was proved by direct comparison with authentic hopenol-b [11, 12].

Compound **1** does not appear to have been previously isolated in nature, though it was derived from three natural triterpenes [11, 13, 14] and was recently biosynthesized by incubating a cell free system from *Acetobacter rancens*, *A. pasteurianum* or *Methylococcus capsulatus* with 2,3-epoxy-2, 3-dihydrosqualene [15–17].

EXPERIMENTAL

Mps were uncorr. Optical rotations were measured in $CHCl_3$ and IR spectra on KBr discs. ^{1}H NMR spectra were recorded at 90 MHz in $CDCl_3$ with TMS as int. standard. EIMS were obtained at 70 eV (probe).

Extraction and isolation of triterpenes. The dried whole herb of *E. supina* (4 kg; collected in Aug. 1976, in the suburbs of Fujiidera City) was extracted with C_6H_6 (5 × 18 l.). The C_6H_6 soln was concd to *ca* 5 l., filtered and then washed with 5% NaOH soln to remove the acidic components. After evacuation of the solvent, the resulting neutral extract (59.4 g) was chromatographed over Si gel (1.5 kg) with a *n*-hexane–C_6H_6 gradient system, beginning with *n*-hexane. Fractions 56–86 (each 300 ml) eluted with *n*-hexane–C_6H_6(1:1) were combined and the resulting gum (1.723 g) was rechromatographed on Al_2O_3 (100 g) with *n*-hexane–C_6H_6 (1:1). Fractions 110–120, eluted after removal of fern-8-en-3β-ol [2], gave a solid mixture (36 mg) inseparable on TLC. Repeated crystallization of the solid from EtOH gave motiol (7 mg).

Concn of the mother soln and recrystallization of the residue from EtOH afforded pure hopenol-b (22 mg).

Motiol. Mp 222–224°, $[\alpha]_D^{21}$ −39.6 (*c* 0.47) (lit. mp 218°, $[\alpha]_D$ −44° [3]); acetate: mp 258–259.5°, $[\alpha]_D^{21}$ −3.2 (*c* 0.33) (lit. mp 247°, $[\alpha]_D$ −3° [3]). This was identified by direct comparison (mmp, IR, ^{1}H NMR and MS) with authentic motiol.

Hopenol-b (**1**). Mp 251–253°, $[\alpha]_D^{21}$ +157.8° (*c* 0.69) (lit. mp 255–261° [3]; mp 233–235°, $[\alpha]_D^{22}$ +153° [14]); IR ν_{max}^{KBr} cm^{-1}: 3610, 1080 (OH), 1638, 982 ($\overset{|}{C}=CH_2$); ^{1}H NMR: δ0.72 (3H, *s*, H-28), 0.76 (3H, *s*, H-24), 0.82 (3H, *s*, H-25), 0.93 (3H, *s*, H-27), 0.98 (6H, *s*, H-23 and H-26), 1.75 (3H, *s*, H-30), 3.19 (1H, *q*, J = 12 and 6 Hz, H-3), 4.78 (2H, *br s*, $W_{1/2}$ = 4.5 Hz, H-29); EIMS *m/z* (rel. int.): 426 $[M]^+$ (6), 411 (5), 393 (5), 383 $[M - C_3H_7]^+$ (4), 378 (5), 370 $[M - Me - C_3H_5]^+$ (4), 315 (7), 207 (39), 204 (16), 189 (100).

Acetylation of **1** (7 mg) with Ac_2O–pyridine (1:1, 2 ml) gave **2** (MeOH–$CHCl_3$), 7 mg, M^+: *m/z* 468 ($C_{32}H_{52}O_2$), IR ν_{max}^{KBr} cm^{-1}: 1738, 1257 (OAc), 1638, 895 ($-\overset{|}{C}=CH_2$); ^{1}H NMR: δ 0.73 (3H, *s*, Me), 0.86 (9H, *s*, 3 × Me), 0.93 (3H, *s*, Me), 0.97 (3H, *s*, Me), 1.77 (3H, *s*, H-30), 2.06 (3H, *s*, OCOMe), 4.52 (1H, *q*, J = 13 and 7 Hz, H-3), 4.83 (2H, *br s*, H-29).

Compound **1** was identified by direct comparison (mmp, IR and MS) with authentic hopenol-b [11, 12].

Oxidation of **1**. Compound **1** (5 mg) in pyridine (2 ml) was oxidized with CrO_3–pyridine (5 mg in 1 ml) at 10° for 7 hr. Chromatography and crystallization of the product gave **3** (MeOH–$CHCl_3$), 3 mg, mp 220–222° (lit. mp 220–221° [11]); M^+: *m/z* 424 ($C_{30}H_{48}O$); IR ν_{max}^{KBr} cm^{-1}: 1702 (C = O), 1638, 892 ($\overset{|}{C}=CH_2$). This showed physical and spectral data identical with hopenone-b [11, 12].

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