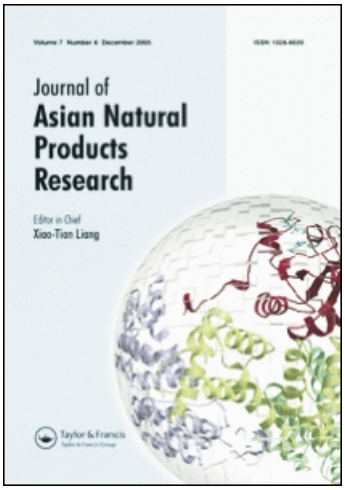

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Sesquiterpenoids from *Hedychium yunnanense* and *Porana discifera*, and the structural revision of two sesquiterpenoids from *Laggera pterodonta*

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A new eudesmane-type sesquiterpenoid, hedytriol (**1**), was isolated from *Hedychium yunnanense* (Zingiberaceae). By means of chemical and spectroscopic methods, the structure of **1** was determined as (−)-7*aH*-eudesmane-1β, 4α, 11-triol. A new *ent*-eudesmane sesquiterpenoid, disciferitriol (**2**), was isolated from *Porana discifera* (Convolvulaceae), which was exactly the enantiomer of hedytriol (**1**). The structures of pterodondiol (**3a**) and pterodontriol B (**3**), previously isolated from *Laggera pterodonta*, were revised on the basis of X-ray diffraction, as well as chemical transformations.

Keywords: *Hedychium yunnanens*; Zingiberaceae; Hedytriol; Sesquiterpenoids; Disciferitriol; *Porana discifera*; Convolvulaceae; Pterodondiol; Pterodontriol B

1. Introduction

Hedychium yunnanense Gangep (Zingiberaceae) and *Porana discifera* Schneid (Convolvulaceae), distributed in Yunnan, China, are two Chinese endemic species [1]. Our previous papers reported the isolation of some diterpenoids, sesquiterpenoids and phytoecdysteroids from these two plants [2–4]. Continuous study on the chemical constituents led to the isolation of a new sesquiterpenoid, hedytriol (**1**) from *H. yunnanense*, and its enantiomer, disciferatriol (**2**) from *P. discifera*. Their structures were determined by spectroscopic analysis, especially 2D NMR experiments and chemical methods.

2. Results and discussion

The HREI-MS of compound **1** gave a molecular ion peak at *m/z* 256.2045 corresponding to the molecular formula $C_{15}H_{28}O_3$, presuming **1** may be a sesquiterpenoid compound.

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The base peak at *m/z* 59 revealed that an oxygenated isopropyl moiety, $Me_2C(OH)$, bore on the molecular skeleton of **1**. ^{1}H NMR spectra of **1** showed the resonance signals of an oxymethine at δ 3.01 (1H, m), four methyls at 0.70 (3H, s), 0.92 (3H, s), 1.02 (3H, s) and 1.04 (3H, s), three hydroxyl groups at 4.26 (1H, d, $J = 4.8$ Hz), 3.95 (1H, s) and 3.91 (1H, s) (table 1), which indicated that two hydroxyl groups were attached to quaternary carbons, and one was attached to a methine carbon. The oxymethine signal at δ 3.01 in ^{1}H NMR spectrum would be simplified to dd peak at δ 3.64 ($J = 5.8$, 9.0 Hz) when the spectrum was performed in C_5D_5N. This observation was further supported the third hydroxyl was attached to the methine carbon C-1 or C-9. ^{13}C NMR (DEPT) showed 15 signals including 4 methyls, 5 methylenes, 3 methines (one of which bearing oxygen) and 3 quaternary carbons (two of which bearing oxygens). These spectral data suggested that the molecular skeleton of **1** was a bicyclic sesquiterpenoid. The ^{1}H NMR and ^{13}C NMR spectra of **1** were similar to those of cryptomeridiol (**1b**) [2,3], indicating that **1** may be a hydroxyl-substituted cryptomeridiol. The key HMBC showed long-range correlation between the hydroxyl proton at δ 4.26 (1H, d, $J = 4.8$ Hz) and C-10 (δ 38.4, s), suggesting that C-1 or C-9 was substituted by hydroxyl group (figure 1). The observation of coupling correlation between H-1 and H-2 in ^{1}H—^{1}H COSY, and the long-range correlation between H-2 and C-4 in HMBC, indicated that C-1 was substituted by hydroxyl group. The β-orientation of 1-OH was confirmed by the coupling constant of H-1. Comparison with those of cryptomeridiol (**1b**), the upfield shift of C-15 of hedytriol (**1**) was observed, due to γ-*gauch* effect of 1β-OH. In addition, **1** was oxidized with PCC in acetone to yield 2-ketone (**1a**) [5], and then **1a** was reduced by Wolf-Khishner-Huang method to afford cryptomeridiol (**1b**) [6], whose ^{1}H NMR, ^{13}C NMR, EI-MS and $[\alpha]_D$ were identical to those of authentic sample (Scheme 1) [7,8]. Therefore, the structure of **1** was unambiguously determined as (−)-7*aH*-eudesmane-1β,4α, 11-triol.

The structure of **1** was elucidated as the so-called 1β-hydroxycryptomeridiol in a previous paper [9]. But a distinct difference between the signals of C-5 and C-7 were observed in ^{13}C NMR spectra, indicating they were not the same compound. Thus, the structure elucidation of the so-called 1β-hydroxycryptomeridiol was incorrect.

The positive high-resolution FAB-MS of compound **2** gave a molecular ion peak at *m/z* 257.2036 corresponding to the molecular formula $C_{15}H_{28}O_3$. Its EI-MS, IR, ^{1}H NMR and

Table 1. ^{13}C NMR data of compounds **1**, **1a**, **2**, **1b** pterodontriol B and pterodondiol[†].

Position	***1***[‡]	***1***	***2***	***1a***	***1b***	*Pterodontriol B [11]*	*Pterodondiol [10]*
1	78.0d	79.5d	79.5d	215.6s	41.8t	80.1d	42.6t
2	28.7t	30.0t	30.4t	35.9t	20.7t	30.1t	20.9t
3	40.7t	42.5t	42.8t	36.6t	44.3t	39.0t	44.4t
4	70.7s	71.7s	71.7s	71.5s	71.2s	71.7s	71.5s
5	52.4d	54.0d	54.0d	53.8d	55.4d	48.2d	49.8d
6	21.0t	22.3t	22.3t	22.8t	22.3t	21.8t	21.8t
7	49.1d	50.0d	50.6d	50.0d	50.9d	42.8d	43.2d
8	21.8t	23.1t	23.1t	22.7t	23.2t	21.9t	21.9t
9	41.0t	42.1t	42.4t	41.1t	45.5t	42.4t	42.6t
10	38.4s	39.8s	40.1s	46.6s	34.8s	39.6s	34.6s
11	69.8s	71.0s	71.0s	70.2s	71.6s	74.0s	73.8s
12	27.0q	27.9q	27.9q	27.8q	28.0q	29.8q	29.8q
13	27.5q	28.0q	28.0q	28.1q	28.0q	30.4q	30.6q
14	22.5q	23.4q	23.4q	24.2q	23.2q	23.1q	22.9q
15	13.3q	14.1q	14.0q	18.2q	19.1q	14.4q	19.4q

[†] ^{13}C NMR spectra were obtained at 125 MHz and recorded in C_5D_5N at room temperature, respectively.
[‡] Recorded in DMSO-d_6 at room temperature.

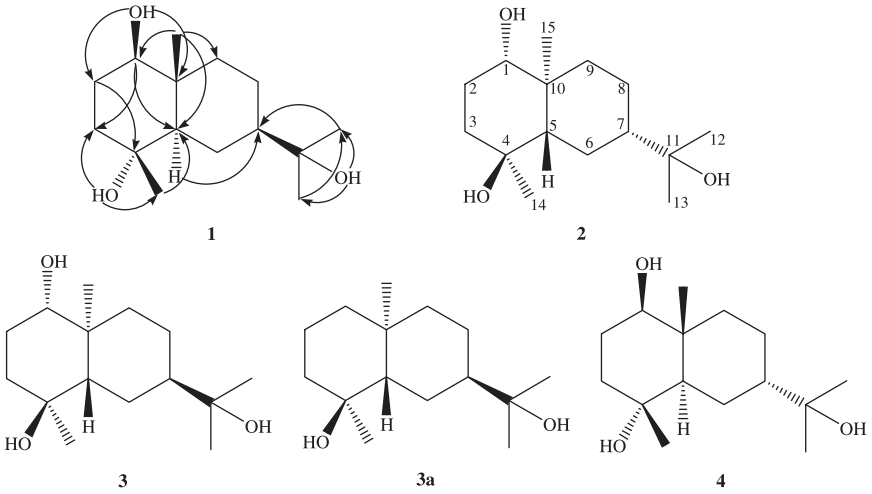
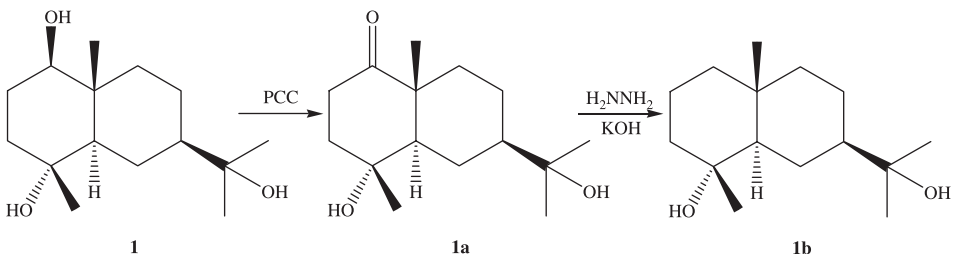


Figure 1. The structures of compounds **1**–**4** and the selected HMBC correlations of hedytriol (**1**).

^{13}C NMR spectra were identical to those of hedytriol (**1**) (table 1). Furthermore, the $[\alpha]_D$ data of **1** and **2** were almost the same, but the direction of the optical rotation was reversed. Thus, the structure of disciferitriol (**2**) could be elucidated as (+)-7β*H-ent*-eudesmane-1α,4β,11-triol (figure 1). But the structure of **2** has been defined as the pterodontriol B from *Laggera pterodonta* [10,11], and the significant difference between the signals of C-5 and C-7 were also observed in ^{13}C NMR spectra, indicating they were not the same compound. The structure elucidation of pterodontriol B was based on the comparison of its NMR spectra with those of pterodondiol [10,11]. In order to examine the validity in the structure determination of pterodontriol B, the structure of pterodondiol was re-examined. Thus, the X-ray diffraction experiments of pterodondiol were performed (figure 2), which revealed that the 7-isopropyl moiety was axial-oriented, opposite to that in the literature. According to the literature [7,8,13], the signal of C-5 and C-7 at *ca.* 54 $\pm$ 2 and *ca.* 50 $\pm$ 1 ppm, and 49 $\pm$ 1 and 42 $\pm$ 1 ppm indicated that the relative configuration of 10-methyl and 7-isopropyl moiety was *cis*- and *trans*-, respectively. Therefore, the structures of pterodontriol B, pterodondiol and the so-called 1β-hydroxycryptomeridiol should be revised as **3**, **3a** and **4**, respectively (figure 1).



Scheme 1. Chemical transformation of hedytriol (**1**).

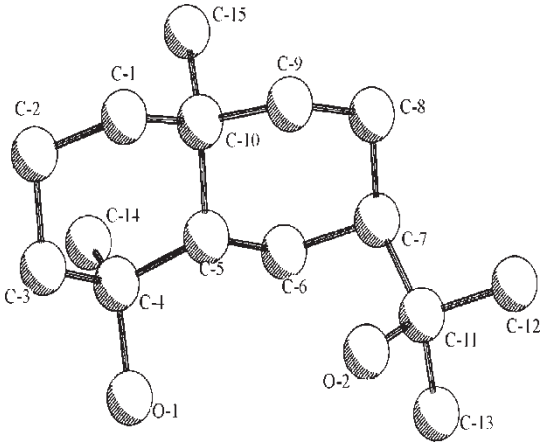


Figure 2. Crystal structure of pterodondiol (**3a**).

3. Experimental

3.1 General experimental procedures

Melting points were measured using XRC-1 micromelting apparatus and are uncorrected. Optical rotations were determined on a JASCO-20C digital polarimeter. IR spectra were measured on a Perkin-Elmer-577 spectrophotometer. HREI-MS, HRFAB-MS and EI-MS were performed on VG Autospec-3000 spectrometer. NMR spectra were recorded on a Brucker AM-400 and a Brucker DRX-500 spectrometer.

3.2 Plant material

The rhizomes of *Hedychium yunnanense* Gangep was collected in Kunming, Yunnan Province of China in September 1993, and the plant was identified by Professor S.Q. Tong, Kunming Institute of Botany. The aerial parts of *Porana discifera* Schneid was collected in Xishuangbanna, Yunnan Province of China in November 1997, and the plant was identified by Professor Ruizheng Fang, Kunming Institute of Botany. The voucher specimens were deposited in Kunming Institute of Botany, Kunming, China.

3.3 Extraction and isolation

The dried and ground rhizomes of *H. yunnanense* (4.0 kg) were extracted three times with 95% EtOH under reflux, and the solvent was evaporated *in vacuo*. The residue (410 g) was partitioned in H_2O and extracted with petroleum ether and BuOH, respectively. The BuOH layer was concentrated *in vacuo* to give 28 g of residue. The BuOH extract was subjected to column chromatography (CC) on silica gel, using EtOAc/MeOH as eluent. Five fractions were obtained. The second fraction was further purified using CC on silica gel with EtOAc as eluent, and recrystallised in EtOAc to afford **1** (116 mg).

The dried and ground aerial parts of *P. discifera* (2.5 kg) were extracted four times with 90% EtOH at room temperature. The extracts were concentrated to the volume (1000 ml) at reduced pressure and then defatted with petroleum ether. The defatted fraction (126 g) was

subjected to flash CC over silica gel eluted with EtOAc, gradient EtOAc-acetone and acetone to separate two parts, phytoecdysteroid and non-phytoecdysteroid that was detected by 3% vanillin in TLC [12]. The non-phytoecdysteroid fraction (46.2 g) was further separated into three fractions by CC over silica gel. The first fraction (5.8 g) was then isolated by flash CC over silica gel to yield **2** (21 mg), eluting with $CHCl_3$/MeOH (10:1).

Hedytriol (**1**) obtained as white, amorphous powder, mp 179–181°C, $[\alpha]_D^{22.9}$ −28.7 (*c* 0.218, MeOH). IR ν_{max}^{KBr} 3414 (OH), 1458, 1445, 1396, 1364, 1079, 911 cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz) δ 3.01 (m, 1H, H-1α), 1.44 (m, 2H, H-2), 1.36 (m, 1H, H-3α), 1.54 (m, 1H, H-3β), 1.05 (dd, 1H, J = 3.9, 12.3 Hz, H-5α), 1.84 (m, 1H, H-6β), 1.09 (m, 1H, H-6α), 1.12 (m, 1H, H-7α), 1.51 (m, 1H, H-8α), 1.02 (m, 1H, H-8β), 0.87 (m, 1H, H-9β), 1.79 (m, 1H, H-9α), 1.02 (s, 3H, H-12), 1.04 (s, 3H, H-13), 0.92 (s, 3H, H-14), 0.70 (s, 3H, H-15), 4.26 (d, 1H, J = 4.8 Hz, 1-OH), 3.95 (s, 1H, 4-OH) and 3.91 (s, 1H, 11-OH). ^{1}H NMR (C_5D_5N, 400 MHz) δ 3.64 (dd, 1H, J = 5.8, 9.0 Hz, H-1α), 2.67 (br.d, 1H, J = 11.8 Hz, H-6α), 2.42 (br.d, 1H, J = 12.6 Hz, H-3α), 1.91–2.04 (m, 4H), 1.48–1.71 (m, 5H), 1.36 (m, 1H, H-6β), 1.38 (s, 3H, H-12), 1.39 (s, 3H, H-13), 1.37 (s, 3H, H-14), 1.22 (s, 3H, H-15). ^{13}C NMR data (DMSO-d_6, 125 MHz and C_5D_5N, 100 Hz), see table 1. EI-MS *m*/*z* $[M]^+$ (0.5), 241 (5), 223 (4), 198 (15), 180 (34), 162 (66), 122 (63), 59 (100). HREI-MS *m*/*z* 256.2045 $[M]^+$ (calcd for $C_{15}H_{28}O_3$, 256.2038).

Disciferatriol (**2**), obtained as a colourless needle (acetone), mp 124–126°C, $[\alpha]_D^{21}$ +27.3 (*c* 0.22, MeOH). IR ν_{max}^{KBr} 3413 (OH), 1460, 1445, 1390, 1361, 1078, 1056, 900 cm^{-1}. ^{1}H NMR (C_5D_5N, 500 MHz) δ 3.63 (dd, 1H, J = 5.7, 9.2 Hz, H-1β), 1.93 (m, 1H, H-2β), 1.45 (d, 1H, J = 7.7 Hz, H-2α), 2.42 (dt, 1H, J = 2.5, 12.6 Hz, H-3α), 1.97 (m, 1H, H-3β), 1.69 (dd, 1H, J = 2.4, 12.0 Hz, H-5β), 2.67 (dd, 1H, J = 2.4, 11.6 Hz, H-6α), 1.38 (m, 1H, H-6β), 2.04 (m, 1H, H-7), 1.52 (m, 2H, H-8), 1.99 (m, 1H, H-9α), 1.48 (m, 1H, H-9β), 1.38 (s, 3H, H-12), 1.39 (s, 3H, H-13), 1.37 (s, 3H, H-14), 1.22 (s, 3H, H-15). ^{13}C NMR data, see table 1. EI-MS *m*/*z* 257$[M + 1]^+$(1), 241 (8), 223 (5), 205 (11), 198 (19), 187 (4), 180 (47), 162 (76), 147 (36), 139 (37), 122 (78), 107 (38), 95 (52), 81 (45), 72 (46), 59 (100). Positive HRFAB-MS *m*/*z* 257.2036 $[M + 1]^+$ (calcd for $C_{15}H_{29}O_3$, 257.2117).

3.4 Chemical transformations

The solution of 90 mg (0.35 mmol) of hedytriol (**1**) in 20 ml of acetone was stirred for 20 min at room temperature (RT), then 270 mg (0.7 mmol) of PCC (pyridnium chlorochromate) was added. The reaction mixture was continuously stirred at RT until **1** was consumed, then 200 ml of water was added and extracted with 200 ml of ethyl acetate. After being dried on anhydrous Na_2SO_4 and evaporated at reduced pressure, the layer of ethyl acetate gave a residue that subjected to flash CC over silica gel to afford **1a** 73 mg (82% yield), eluting with 1:1 petroleum ether/EtOAc. 63 mg (0.25 mmol) of **1a** was dissolved in 10 ml of glycol and the solution was stirred for 20 min at RT. Then 45 mg (0.8 mmol) of KOH and 6 ml of 87% hydrazine hydrate were added and the mixture allowed to reflux for 2 h. The excess of hydrazine hydrate and the produced water were distilled off. When the temperature reached 170°C, the reaction mixture was left to reflux for 3 h at this temperature, then 60 ml of water was added at RT and extracted with 100 ml of ethyl acetate. After being dried on anhydrous Na_2SO_4 and evaporated at reduced pressure, the layer of ethyl acetate afforded a solid which subjected to flash CC over silica gel to provide for cryptomeridiol (**1b**) 45 mg (75% yield), eluting with 2:1 (v/v) petroleum ether/EtOAc.

Compound **1a** obtained as white, amorphous powder, $[\alpha]_D^{22}$ −24.5 (*c* 0.37, MeOH). ^{1}H NMR (C_5D_5N, 500 MHz) δ 2.55 (m, 1H, H-2α), 1.55 (m, 1H, H-2β), 2.65 (d, 1H, $J = 11.0$ Hz, H-3α), 2.12 (d, 1H, $J = 11.0$ Hz, H-3β), 1.89 (dd, 1H, $J = 3.1$, 11.9 Hz, H-5β), 2.71 (dd, 1H, $J = 7.6$, 11.8 Hz, H-6β), 1.58 (m, 1H, H-6α), 2.04 (m, 1H, H-7β), 1.53 (m, 2H, H-8), 1.48 (m, 1H, H-9β), 2.08 (m, 1H, H-9α), 1.35 (s, 3H, H-12), 1.34 (s, 3H, H-13), 1.48 (s, 3H, H-14), 1.16 (s, 3H, H-15). ^{13}C NMR data, see table 1. EI-MS *m/z* $[M]^+$254 (27), 236 (16), 221 (9), 196 (68), 178 (77), 163 (55), 135 (52), 123 (74), 109 (42), 95 (66), 81 (53), 71 (47), 59 (100).

Cryptomeridiol (**1b**) obtained as white, amorphous powder, $[\alpha]_D^{26}$ −68.8 (*c* 0.16, $CHCl_3$). ^{1}H NMR (C_5D_5N, 500 MHz) δ 1.56 (m, 1H, H-1α), 1.22 (m, 1H, H-1β), 1.76 (m, 2H, H-2), 1.84 (d, 1H, $J = 12.2$ Hz, H-3β), 1.51 (m, 1H, H-3α), 1.45 (dd, 1H, $J = 4.1$, 12.4 Hz, H-5β), 2.63 (d, 1H, $J = 12.4$ Hz, H-6β), 1.53 (m, 1H, H-6α), 1.59 (m, 1H, H-7α), 1.09 (m, 1H, H-8β), 1.98 (d, 1H, $J = 12.4$ Hz, H-8α), 1.64 (m, 1H, H-9β), 1.31 (d, 1H, $J = 12.8$ Hz, H-9α), 1.37 (s, 3H, H-12), 1.36 (s, 3H, H-13), 1.29 (s, 3H, H-14), 0.92 (s, 3H, H-15). ^{13}C NMR data, see table 1. EI-MS *m/z* 225$[M - 15]^+$ (6), 207 (9), 189 (16), 182 (20), 164 (59), 149 (100), 135 (24), 123 (42), 109 (56), 95 (38), 81 (39), 71 (41), 59 (92), 43 (86).

Pterodondiol (**3a**), colourless needle, mp 110–112°C, $[\alpha]_D^{26}$ +24.8 (*c* 0.22, $CHCl_3$). ^{1}H NMR (C_5D_5N, 500 MHz) δ 1.31 (m, 1H, H-1α), 1.51 (m, 1H, H-1β), 1.46 (m, 2H, H-2), 1.74 (m, 1H, H-3α), 1.66 (m, 1H, H-3β), 2.03 (dd, 1H, $J = 3.8$, 13.7 Hz, H-5β), 2.91 (d, 1H, $J = 13.4$ Hz, H-6β), 1.37 (m, 1H, H-6α), 1.71 (m, 1H, H-7β), 1.68 (m, 1H, H-8β), 1.59 (m, 1H, H-8α), 1.11 (m, 1H, H-9β), 1.29 (dd, 1H, $J = 3.6$, 12.8 Hz, H-9α), 1.23 (s, 3H, H-12), 1.21 (s, 3H, H-13), 1.02 (s, 3H, H-14), 0.84 (s, 3H, H-15). ^{13}C NMR (C_5D_5N, 125 MHz) δ 41.6 (t, C-1), 20.2 (t, C-2), 43.6 (t, C-3), 72.6 (s, C-4), 48.8 (d, C-5), 20.6 (t, C-6), 41.9 (d, C-7), 21.4 (t, C-8), 41.6 (t, C-9), 34.3 (s, C-10), 74.7 (s, C-11), 29.6 (q, C-12), 29.8 (q, C-13), 21.9 (q, C-14), 18.5 (q, C-15). EI-MS *m/z* 222$[M - 18]^+$ (10), 204 (13), 189 (68), 164 (55), 149 (26), 135 (52), 123 (80), 109 (42), 95 (56), 81 (53), 71 (61), 59 (100).

3.5 X-ray structure determination of pterodondiol (3a)

The crystal adopted in the X-ray diffraction experiment was the monoclinic and 0.20 × 0.20 × 0.30 mm large. Its special point group was $P2_1$ and the parameters of the unit cell were $a = 15.9670$ (13), $b = 11.9640$ (10), $c = 16.8300$ (10) Å and $\beta = 71.525$ (5) °. The volume of the unit cell was 3021.3 (4) $Å^3$ in which there were 2 pieces of molecule ($Z = 2$). X-ray diffraction intensity data of **3a** were collected on a MAC DIP-2030K diffractometer with graphite-monochromater Mo Kα radiation ($\lambda = 0.71073$ Å) by the ω scan technique (scan width 0–180°, $2\theta \leq 50°$]. Altogether 5016 reflections were collected, of which 4893 with $|F|^2 \geq 8\sigma\ |F|^2$ were observed. The structure was solved by direct methods and refined by block-matrix least-squares procedure to $R_f = 0.064$, $R_w = 0.058$. Hydrogen positions were found from difference Fourier maps and geometric calculations. All calculations were carried out on a personal computer using the SHELX-86 program system. The obtained molecular formula, molecular weight and crystal density was $C_{15}H_{28}O_2$, 240.39 and 1.057 g/ml, respectively.

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