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# 3-CAREN-5-ONE FROM *KAEMPFERIA GALANGA*

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**Key Word Index**—*Kaempferia galanga*; Zingiberaceae; monoterpene ketone; 3-caren-5-one.

**Abstract**—The rhizomes of *Kaempferia galanga* afforded a new monoterpene ketone whose structure was elucidated as 3-caren-5-one by spectroscopic means.

## INTRODUCTION

Rhizomes of *Kaempferia galanga* L. have been traditionally used as a stomachic and an incense [1]. Along with the constituents hitherto reported such as ethyl cinnamate, ethyl *p*-methoxycinnamate and *p*-methoxycinnamic acid [2, 3], we isolated a new monoterpene ketone (compound 1).

## RESULTS AND DISCUSSION

Compound **1** is a colourless oil with a molecular formula of $C_{10}H_4O$. Its IR (1630 $cm^{-1}$) and $^{13}C$ NMR ($\delta$196.3, 158.6, 126.4) spectra suggested the presence of an enone moiety which was supported by the formation of a dark red coloured 2,4-dinitrophenylhydrazone (mp 107–109°). The $^1H$ NMR spectrum showed three singlet methyl signals ($\delta$1.03, 1.18, 1.87) suggesting the presence of two quaternary methyl groups and an olefinic one. The latter ($\delta$1.87) has four fine splittings which changed to three on irradiation of the broad singlet olefin signal at $\delta$5.80 revealing the existence of long-range coupling between these protons. Signals centered at $\delta$2.28 and 2.65 changed to an AB type coupling pattern ($J = 22$ Hz) on irradiation of the one proton signal at $\delta$1.43, thus indicating the presence of an ABX spin system. The presence of long-range coupling between the olefinic methyl ($\delta$1.87) and the methylene ($\delta$2.28, 2.65) protons was confirmed by selective irradiation of each signal. These evidences link the enone moiety and the ABX spin system into a partial structure (**2**).

In addition to the above signals, the $^{13}C$ NMR spectrum of compound **1** showed the presence of one quaternary carbon and two methine carbons. This enabled us to assign a bicyclo[4.1.0]heptane ring system for this compound. Chemical shifts of the three methyl carbons of compound **1** were very similar to those of 3-carene ($\delta$13.2, 23.6, 28.4) [4]. From these data, we concluded that compound **1** is 3-caren-5-one (4,7,7-trimethylbicyclo[4.1.0]hept-3-en-2-one) (**1**) [5]. To our present knowledge, this is the first report of the isolation of the compound from a natural source.

## EXPERIMENTAL

Cut rhizomes of *K. galanga* (2 kg) were extracted × 3 with MeOH for 2 hr under reflux. The MeOH extract, after concn to *ca* 300 ml under red. pres. was extracted with 4 × 200 ml portions of hexane. The residual MeOH layer was concd to dryness and partitioned between $CHCl_3$–MeOH–$H_2O$ (6:3:2) to give 16.63 g of a $CHCl_3$ sol. fraction. A portion (6.61 g) of this fraction was subjected to silica gel CC and eluted with $C_6H_6$, $C_6H_6$–$Me_2CO$ (9:1), and $C_6H_6$–$Me_2CO$ (4:1), successively. The $C_6H_6$ and $C_6H_6$–$Me_2CO$ (9:1) eluates gave Et cinnamate and Et *p*-methoxycinnamate. The later part of the $C_6H_6$–$Me_2CO$ (4:1) eluate gave *p*-methoxycinnamic acid. The earlier part (680 mg) of the $C_6H_6$–$Me_2CO$ (4:1) fraction was repeatedly chromatographed on silica gel to yield a fraction (75 mg) containing compound **1**. This fraction was purified by medium pressure LC on LiChroprep Si-60 eluting with $C_6H_6$–EtOAc (19:1) to give 23 mg of compound **1** as a colourless oil. IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 1630 (enone); EIMS (probe) 20 eV *m/z* (rel. int.): 150 $[M]^+$ (8). $^1H$ NMR (100 MHz, $CDCl_3$): $\delta$1.03 (3H, *s*, H-8), 1.18 (3H, *s*, H-9), 1.43 (1H, *td*, $J = 7$, 1.4 Hz, H-6), 1.55 (1H, *br d*, $J = 7$ Hz, H-1), 1.87 (3H, *br s* with four fine splittings, H-10), 2.28 (1H, *br d*, $J = 22$ Hz, H-5), 2.65 (1H, *dd*, $J = 22$, 7 Hz, H-5), 5.80 (1H, *br s* with fine splittings, H-3). $^{13}C$ NMR (25 MHz, $CDCl_3$): $\delta$196.3 (*s*, C-2), 158.6 (*s*, C-4), 126.4 (*d*, C-3), 32.8 (*d*, C-1), 28.4 (*q*, C-9), 27.9 (*t*, C-5), 25.8 (*d*, C-6), 23.6 (*q*, C-10), 22.5 (*s*, C-7), 14.4 (*q*, C-8). 2,4-Dinitrophenylhydrazone, dark red prisms from EtOH, mp 107–109°. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1335, 1520, 1585, 1618.

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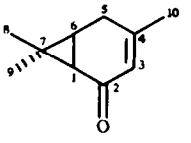
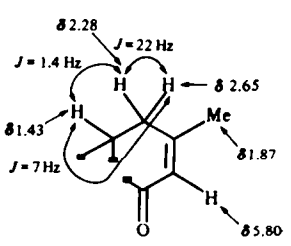


**1**




**2**

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# A DIMER OF *d*-PINOCARVONE FROM *CEDRONELLA CANARIENSIS*

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**Key Word Index**—*Cedronella canariensis*; Labiatae; terpenes, *d*-pinocarvone, dimer of *d*-pinocarvone; cedronellone; ursolic acid.

**Abstract**—From the aerial parts of *Cedronella canariensis* a dimer of *d*-pinocarvone, cedronellone, has been isolated, together with large amounts of *d*-pinocarvone and ursolic acid. The structure of cedronellone was established by chemical and spectroscopic means.

## INTRODUCTION

*Cedronella canariensis* Webb. & Berth. (Labiatae) is a plant endemic to the Canary and Madeira Islands [1], the chemical study of which has not been previously carried out. From the aerial parts of this species we have isolated large amounts of the monoterpene *d*-pinocarvone (**1**, 0.74% on dry plant) [2] and ursolic acid (1.42%), besides minor quantities of a dimer of *d*-pinocarvone (**2**, cedronellone, 0.1%) not previously described as synthetic or natural product.

## RESULTS AND DISCUSSION

Cedronellone (**2**) had a molecular formula $C_{20}H_{28}O_2$ and its IR spectrum showed ketone (1728 $cm^{-1}$) and enol-ether (1690 $cm^{-1}$, strong) absorptions. The $^1H$ and $^{13}C$ NMR spectra of compound **2** revealed four methyl groups (C-Me singlets at $\delta$1.38, 1.25, 0.90 and 0.79, and carbon atom resonances at $\delta$27.33, 25.95, 22.13 and 20.54, all quartets in the spectrum recorded under SFORD conditions), a ketone function ($\delta$208.53, *s*), a fully substituted enol-ether grouping (no signals of olefinic protons, carbon atom resonances at $\delta$142.46, *s*, and 112.26, *s*), a fully substituted carbon atom bearing an oxygen atom ($\delta$80.33, *s*), six methylene and four methine groupings and, finally, two quaternary carbon atoms (see Experimental).

Distillation of cedronellone (**2**) under vacuum quantitatively yielded *d*-pinocarvone (**1**) [2], thus establishing that compound **2** was a dimer of this monoterpenoid.

The *R* stereochemistry of the C-2′ centre of cedronellone (**2**) was established as follows. Reduction of compound **2** with sodium borohydride gave a mixture of two epimeric alcohols (**3** and **4**), one of which (**3**) was an extremely unstable substance which was quantitatively transformed into another compound (**5**) in the extraction process of the reaction (see Experimental). The structure of the derivative **5** was in agreement with its spectroscopic data [IR: no hydroxyl absorption; $^{13}C$ NMR: carbons bearing oxygen atoms at $\delta$105.92, *s* (C-3), 81.66, *s* (C-2′) and 75.38, *d* (C-3′), see also Experimental]. On the other hand, application of the Horeau's method [3] to the alcohol **4** established as *R* the absolute configuration of its hydroxyl function.

All the above facts were only compatible with a 2′*R* configuration of cedronellone (**2**), since the 3′*S*-hydroxy derivative (**3**), which possesses a *cis* relationship between the hydroxyl group and the ethereal oxygen atom, was transformed into the tetrahydropyran **5**. In compound **4**, with a 3′*R* configuration in a *d*-pinocarvone hydrocarbon skeleton, its hydroxyl group is *trans* with respect to the ethereal oxygen atom, thus excluding the possibility of the formation of a tetrahydropyran derivative.

It is reasonable to assume that cedronellone (**2**) can be formed from *d*-pinocarvone (**1**) by a hetero-Diels–Alder reaction. This assumption was also in agreement with a 2′*R* configuration for compound **2**, since it is known [4]

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