Notes

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A New Thymol Derivative from *Pulicaria undulata*

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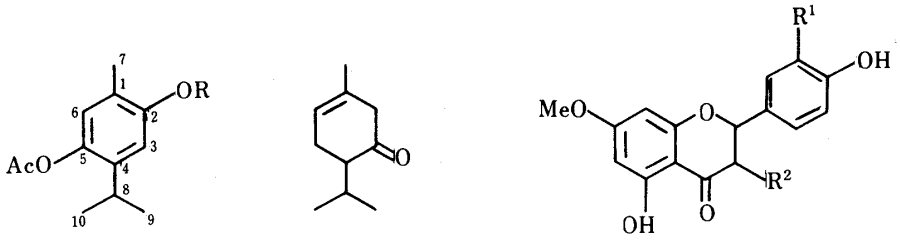
A new 2-hydroxyacetylthymol derivative was isolated from *Pulicaria undulata*. Its structure was determined by spectroscopic methods.

Keywords——*Pulicaria undulata*; Compositae; Inulae; 2-hydroxyacetylthymol

Several species of the genus *Pulicaria* (Compositae, tribe Inulae), placed in the subtribe Inulinae, have been investigated chemically.[1] In addition to widespread polyacetylenes,[2] thymol derivatives[2] and flavones,[3-5] caryophyllane derivatives were recently isolated.[6] We studied the constituents of *Pulicaria undulata*, as a continuation of our chemical investigations of some important Egyptian plants belonging to Compositae.[7] Our findings are reported here.

The aerial parts of the plant gave a new thymol derivative (Ia), in addition to other known substances, which are lupeyl acetate, taraxasteryl acetate, a ketonic product (II) and two flavonoids (III, IV). The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of Ia indicated the resence of an isopropyl group (two doublets at δ 1.13). An aromatic methyl signal appeared at δ 2.17. The oxygen functions were deduced to be phenolic and acetyl groups. The chemical shifts of the aromatic proton signals also agreed with the proposed substitution pattern (see Experimental). The infrared (IR) spectrum of Ia showed a well-defined band at 3600 cm^{-1} (free OH) in addition to a carbonyl band at 1750 cm^{-1}. Further evidence for structure Ia was gained from the mass spectrum (MS) (M$^+$ 208.109), and acetylation with acetic anhydride to give Ib. The ^{1}H-NMR spectrum (400 MHz) of Ib showed that the signal of the aromatic methyl group was shifted slightly (δ 2.19), and the new signal due to the acetyl group appeared at δ 2.21. The signals for the isopropyl group were unchanged (see Experimental).



Ia : R=H
Ib : R=Ac

II

III : R^1=H, R^2=OH
IV : R^1=OH, R^2=H

Chart 1

The known ketonic product II, which we isolated from *Pulicaria* species, was reported recently by Sacco *et al.* They determined its structure basically by analysis of the ^{1}H-NMR spectrum.[8] The flavonoid components of *Pulicaria* were identified as 7-*O*-methylaramanderin (III) and its isomer IV. These two flavonoids (III, IV) were isolated previously from *Eupatorium* species.[9] The isolated compounds were identified by comparison of their IR, ^{1}H-NMR and MS with those of authentic samples.

Experimental

Isolation of Compounds I—IV——The air-dried plant material (150 g), collected from Wadi Qena, Egypt, in April 1984, was extracted with ether: pet. ether (40—60 °C): methanol = 1 : 1 : 1. The extract of the aerial parts was first treated with methanol to remove long-chain hydrocarbons and then partially separated by column chromatography (SiO_2) with pet. ether (40—60 °C) containing increasing amount of ether and finally ether: methanol = 10 : 1. The fraction obtained with 10% ether was subjected to repeated thin-layer chromatography (TLC) with pet. ether–ether (9 : 1) to give lupeyl acetate (5 mg) (*Rf* 0.7), taraxasteryl acetate (5 mg) (*Rf* 0.6) and II (3 mg) (*Rf* 0.5). The fraction obtained with 25% ether gave, on repeated TLC with pet. ether–ether (9 : 1), II (2 mg) (*Rf* 0.5) and Ia (5 mg) (*Rf* 0.45). The fraction obtained with methanol : ether = 1 : 10 gave, on repeated TLC with pet. ether–ether (1 : 4), III (10 mg) (*Rf* 0.7, mp 183 °C) and IV (7 mg) (*Rf* 0.55, mp 90 °C).

2-Hydroxyacetylthymol (Ia)——Colorless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1750 (CO). MS *m/z* (rel. int): 208.109 (M^+) (19%) (Calcd. for $C_{12}H_{16}O_3$: 208.109), 165 ($208-C_3H_7$)$^+$ (7%), 151 (100%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.83 (s, H-3), 6.69 (s, H-6), 2.17 (s, Me), 2.9 (qq, H-8), 1.13 (d, H-9 and H-10), 2.29 (s, OAc) (*J*: 8,9 = 8 Hz, 10 ≃ 7 Hz.

2,5-Diacetylthymol (Ib)——Colorless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 and 1765 (CO). MS *m/z* (rel. int): 250.28 (M^+) (3%) (Calcd. for $C_{14}H_{18}O_4$: 250.28), 208 (250 − ketene)$^+$ (18%), 166 (208 − ketene)$^+$ (100%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.74 (s, H-3), 6.69 (s, H-6), 2.19 (s, Me), 2.9 (qq, H-8), 1.13 (d, H-9 and H-10), 2.29 (s, C_5-OAc), 2.21 (s, C_2-OAc) (*J*:8,9 = 8 Hz, 10 ≃ 7 Hz).

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