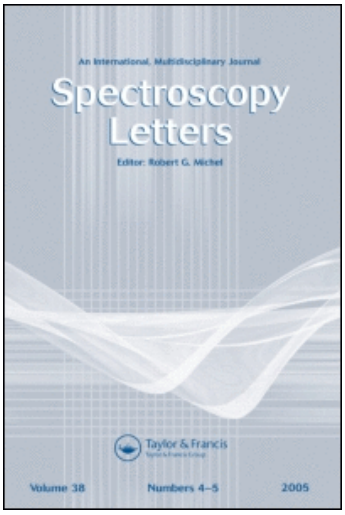

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^{13}C NMR Spectra of Santonin Photoproducts: Characterization of a Novel Product

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^{13}C NMR Spectra of Santonin Photoproducts: Characterization of a Novel Product

Key Words: Santonin, Photoproducts, ^{13}C NMR Spectrum

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ABSTRACT

^{13}C NMR spectra of lumisantonin (2), isosantoxane (3a), its acetyl derivative (3b) and santonic acid (4) are reported. The structure of a novel photo derivative (6) is established on the basis of spectroscopic methods, particularly ^{13}C NMR spectra.

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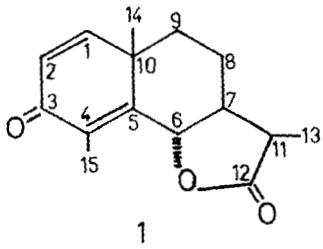
INTRODUCTION

Santonin (1) undergoes a number of interesting photochemical rearrangements which are solvent dependent. Thus irradiation of 1 in dioxane yields lumisantonin (2)[1,2], where as isosantoxane (3a), its acetyl derivative (3b) and santonic acid (4) are the products if irradiation is carried out in aqueous acetic acid[3]. Ethers of the type (3c) and mazdasantonin (5) are further photoproducts of lumisantonin.



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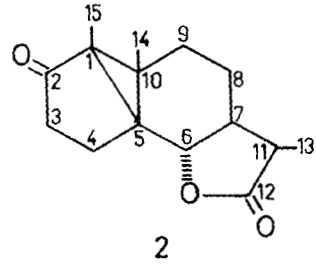

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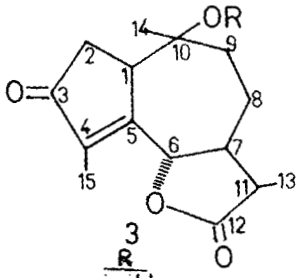


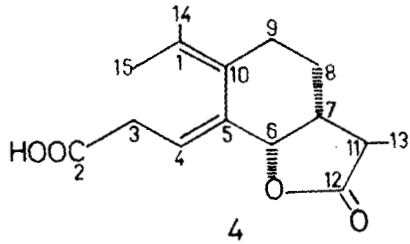
3

R

a: H

b: $COCH_3$

c: CH_3



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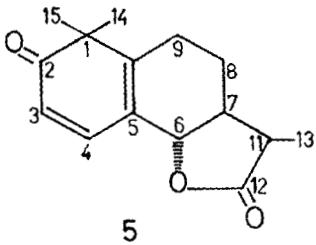

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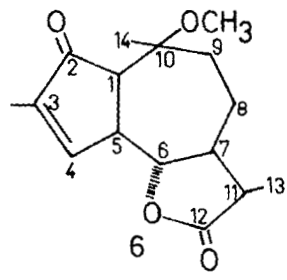


6

Although these product have been known for a long time, there is no record of systematic studies on their ^{13}C NMR spectra. Pregosin et al.[4] have reported the ^{13}C NMR spectra of santonin, 3c and 5. We report here in the ^{13}C NMR spectra of 2-4 and 6 which are given in Table 1. Assignments of the carbon chemical shifts in the ^{13}C NMR spectra were made by the use of the COSY and HETCOR technique[5,6] and by comparison with ^{13}C NMR spectral data of the santonin derivatives

EXPERIMENTAL

Melting points are uncorrected, ^{1}H NMR spectra were recorded on Jeol JNM FX-100 spectrometer. ^{13}C NMR spectra were recorded at 25 MHz and ^{1}H NMR were run at 100 MHz. All the spectra were recorded at 25°C. The compounds were studied for approximately 25 mg per ml solutions in $CDCl_3$. Chemical shift data of the NMR spectra were determined relative to the internal standart TMS.A Hanovia medium pressure lamp was used for the photochemical reaction.

Photochemistry of santonin in acetic acid: Water (4:5)

This was done according to the method of Barton et al.[3] and compounds 3 and 4 were isolated according to the same procedure.

Preparation of neoiso-santoniclactone methylether (10-methoxy-2-oxoguai-3-en-6:12-olide) (6)

To a solution of santonin (0.5 g) in $CHCl_3$ (20 ml) was added maleic anhydride (0.2 g) and minimum amount of MeOH to dissolve it. The solution was irradiated in a quartz flask with a Hanovia 125 W lamp for 7 hrs. The solvent was removed under reduced pressure and the residue chromotographed over flash silica gel (100 g) and eluted first with benzene and then with

Table 1. ^{13}C NMR data for compounds 2,3a,3b,4 and 6 (in $CDCl_3$)

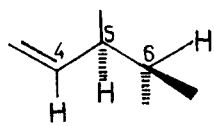
Carbon No	2	3a	3b	4	6
1	50.10 s	48.38 d	47.30 d	140.20 s	48.49 d
2	206.54 s	37.28 t	36.81 t	178.59 s	202.43 s
3	131.31 d	208.20 s	206.83 s	33.75 t	135.91 s
4	157.60 d	142.72 s	143.25 s	110.31 d	153.99 d
5	40.41 s	161.86 s	160.74 s	127.51 s	45.03 d
6	77.60 d	81.50 d	81.20 d	83.30 d	82.07 d
7	48.70 d	50.55 d	48.31 d	54.20 d	54.18 d
8	22.50 t	21.20 t	20.02 t	19.96 t	25.59 t
9	29.62 t	45.14 t	37.89 t	30.41 t	33.58 t
10	42.71 s	74.26 s	85.38 s	130.92 s	79.26 s
11	41.20 d	41.39 d	41.39 d	42.21 d	42.21 d
12	178.54 s	177.36 s	176.94 s	177.59 s	177.80 s
13	12.51 q	12.44 q	12.44 q	12.45 q	12.79 q
14	17.23 q	25.83 q	25.36 q	22.13 q	25.59 q
15	7.54 q	9.45 q	9.51 q	27.41 q	22.48 q
$\underline{CH_3}CO$			22.40 q		
$CH_3\underline{CO}$			170.30 s		
$O\underline{CH_3}$					56.10 q

benzene:chloroform (1:1);6 was obtained in 73% yield. It was recrystallized from n-Hexane to give white crystals (Yield 71%). mp.164°C.

IR (cm^{-1}): 3020,2985,2900,1775,1685,1160,1070,1020; ^1H NMR($CDCl_3$): δ 1.16(d,j=7.1 Hz,3H),1.34(s,3H),1.56(s,3H),1.60-2.15 (complex signal integrated for 5 protons),2.3(bq,H-11),3.1(s,3H), 3.25(bd,j=3.2 and 5.8 Hz, H-5),4.98(bd,j=5.8 and 9.7 Hz,H-6),7.5 (d,j=3.2 Hz, H-4).For ^{13}C NMR see Table 1.

RESULTS AND DISCUSSION

The photoproducts 3a,b and 4 were obtained by known procedures[1,3]. When the irradiation of 1 was carried out in $CHCl_3$: MeOH in the presence of maleic anhydride, a novel compound named neoiso-santoniclactone methylether (6) was obtained which is an isomer of 3c. The IR spectrum of compound 6 showed two carbonyl bands, one for the carbonyl in the five membered lactone ring (1775 cm^{-1}) and the other (1685 cm^{-1}) indicating a carbonyl group in the cyclopentenone ring. Such latter carbonyl is easily recognized from its resonance (δ 202.43) in the ^{13}C NMR spectrum of 6 (Table 1). The ^{1}H NMR spectrum of 6 was very helpful in the structure elucidation of this compound. This spectrum in $CDCl_3$ (100 MHz) showed signals for 3 protons of the olefinic methyl (δ 1.56,s),14-Me (δ 1.34,s),13-Me (δ 1.16.6,j=7.1 Hz) and protons of the methoxy group at δ 3.1.In addition, H-6 resonates at δ 4.88(bd, j=5.8 and 9.7 Hz), the olefinic proton at δ 7.5(d,j=3.2 Hz) and a multiplet signal (bd,j=3.2 and 5.8 Hz) centred at δ 3.25 which was attributed to H-5. Spin decoupling experiments allowed the assignments of the signals of H-4 (olefinic) through H-6, starting with irradiation of H-5 signal (δ 3.25), which render the signal of H-6 as doublet (j=9.7 Hz) and the signal of the olefinic proton collapses to a singlet. Irradiation of the signal at δ4.98(H-6) affects the signal of H-5, which appears now as a poorly resolved douplet (j=3.0 Hz), while the resonance of the olefinic proton (H-4) remains unaffected. It is clear now from the value of the coupling constants of these protons that the following partial structure can be noticed:



The ^{13}C NMR spectrum of 6 corroborates well the suggested structure and reveals a total of 16 signals due four methyls, two methylenes, four methines, one trisubstituted double bond, two carbonyls and two oxygen bearing H-C-O and -C-O carbons the assignments of all the carbons in 6 were made by the use of COSY, HETCOR and by comparison with the spectral data of other derivatives of santonin.

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