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SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF 1*H*-NAPHTHO[2,1,8-*mna*]XANTHEN-1-ONE AND ITS 8-METHOXY DERIVATIVE

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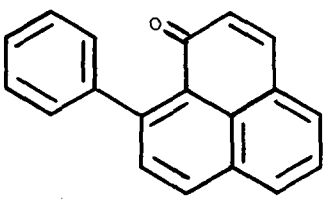
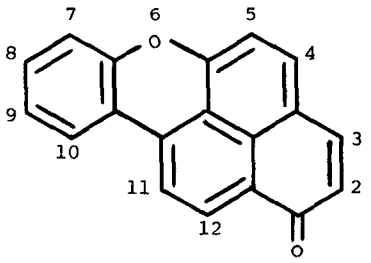
Plants of the botanical family Haemodoraceae contain pigments which are derivatives of 9-phenylphenalenone (1). General methods for the synthesis of these compounds have been described recently[1-3]. Edwards and Weiss[4,5] have also isolated from *Lachnanthes tinctoria* Ell. a new kind of pigment, lachnanthofluorone, which they identified as 2,5-dihydroxy-1*H*-naphtho-[2,1,8-*mna*]xanthen-1-one. It was been reported that pigments of this class are also found in related plant species[1] but the structures of these have not been published. There is an obvious structural, and probably a biogenetic relationship between the two classes of pigments and it has been shown that two of the phenylphenalenones undergo photochemical conversion to naphtho-xanthenones in low yield[4].



(1)



(2)

To provide some model compounds for spectroscopic comparison we have developed two methods for the synthesis of naphthoxanthenones which should be generally applicable to the preparation of natural pigments of this class. Both methods involve cyclisation of suitable phenylphenalen-ones. We report here the first preparation of the parent chromophore 1*H*-naphtho[2,1,8-*mna*]-xanthen-1-one (2) and of its 8-methoxy derivative.

2,7-Dimethoxy-1-naphthaldehyde and 2-methoxyacetophenone were converted in two steps into 3-(2,7-dimethoxy-1-naphthyl)-1-(2-methoxyphenyl)propan-1-one, m.p. 79-80°, in 74% overall yield. Treatment of this ketone with polyphosphoric acid gave directly 6-methoxy-7-(2-methoxyphenyl)-phenalenone, m.p. 144°, in 20% yield. In boiling HBr-acetic acid (45%) this was converted into

the naphthoxanthenone (2) which crystallized from methanol in fine red needles, m.p. 226°, in 60% yield. The same product was also obtained in about 11% yield by a novel oxidative cyclisation of 6-hydroxy-7-(or 9)-phenylphenalenone[6] with VOF_3 in trifluoroacetic acid.

In methanol the naphthoxanthenone (2) absorbs at λ_{max} (log ε) 522 sh (4.23); 493 (4.32); 464 sh (4.17); 366 (3.64); 345 (3.89); 330 (3.86); 299 (3.87); 280 (4.15); 269 (4.00); 244 (4.57); 225 (4.57); 211 sh (4.43). After addition of two drops of conc. HCl to the solution the spectrum changed to λ_{max} (log ε) 513 (4.62); 416 (4.09); 349 (3.89); 322 (3.91); 310 (3.89); 287 (3.88); 271 sh (4.16); 254 (4.55); 217 (4.55). N.m.r. δ($CDCl_3$) 6.79, d, 9.5 Hz, H 2; 7.17, d, 8 Hz, H 5; 7.20-7.54, m, 3H; 7.77, d, 9.5 Hz, H 3; 7.80, d, 8 Hz, H 4; 8.02, d, 8 Hz, H 11; 8.10, bd, 8 Hz, H 9; 8.76, d, 8 Hz, H 12. Decoupling experiments support these assignments. I.R. ν_{max} (KBr) 1638, 1620 cm^{-1}.

Treatment of 6-methoxy-7-(2,4-dimethoxyphenyl)phenalenone, m.p. 174°, with hot HBr-acetic acid produced 8-methoxy-1*H*-naphtho[2,1,8-*mna*]xanthen-1-one, m.p. 248°, in 20% yield. In methanol this compound absorbs at λ_{max} (log ε) 525 (4.38); 495 (4.41); 467 sh (4.19); 394 sh (3.56); 376 (3.73); 350 (3.76); 337 sh (3.63); 305 (3.63); 294 sh (3.67); 260 sh (4.45); 248 (4.57); 221 (4.46). With two drops of conc. HCl added to the solution the spectrum changed to λ_{max} (log ε) 516 (4.89); 482 sh (4.30); 440 (3.79); 350 (3.51); 314 (3.44); 291 sh (3.83); 267 (4.61); 219 (4.45). N.m.r. δ($CDCl_3$) 3.90, s, OCH_3; 6.79, d, 9.5 Hz, H 2; 6.84, bs, H 7; 6.89, dd, J 8 and 2.5 Hz, H 9; 7.14, d, 8 Hz, H 5; 7.75, d, 9.5 Hz, H 3; 7.78, d, 8 Hz, H 4; 7.90, d, 8 Hz, H 11; 7.98, d, 8 Hz, H 10; 8.75, d, 8 Hz, H 12. Assignments of these proton chemical shifts were checked by decoupling experiments. I.R., ν_{max} 1638, 1613 cm^{-1}. All compounds gave satisfactory analytical figures.

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