A NEW DIMERIC DERIVATIVE OF ETHOXYQUIN FROM ITS REACTION WITH ALKYLPEROXY RADICALS

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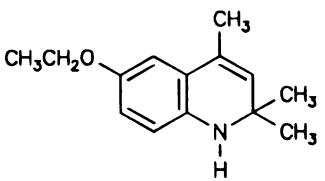
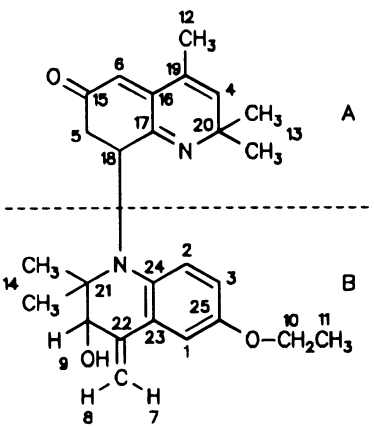
The structure of a new compound formed in the reaction of ethoxyquin with alkylperoxy radicals was resolved by ^{1}H and ^{13}C NMR spectroscopy (including COSY, NOESY, HHC RCT and SSLR INEPT techniques) and confirmed by mass spectrometry. The structure suggests participation of 4-methyl group of ethoxyquin in the deactivation of peroxy radicals. A mechanism of this reaction is proposed.

The importance of ethoxyquin, 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline (*I*) as an antioxidant, antifatigue agent and antiozonant gives a strong impetus to the studies of its stabilizing action. In a comprehensive model study of the reaction of ethoxyquin with peroxy radicals[1], a blue compound (m.p. 192 – 194 °C) was isolated among several other products. On the basis of its NMR and mass spectra, we propose structure *II* for this compound and suggest a new path in manifold reactions of ethoxyquin with peroxy radicals.



I



II

EXPERIMENTAL

^1H and ^{13}C NMR spectra were measured in $(CD_3)_2CO$ solution on a Bruker AC 300 spectrometer at 300 and 75 MHz, respectively. The internal standard was HMDS which is shifted to TMS 0.05 ppm in ^1H and 0.2 ppm in ^{13}C region, respectively. COSY (ref.[2]) as well as NOESY (ref.[3]) spectra were measured with 2 048 points and 512 increments, the mixing delay in NOESY being 0.9 s. HHC RCT spectra[4] were measured with 8 192 points, 128 increments (zero filling to 256) and 3 000 scans; the H–H and H–C evolution delays were 20 ms and 4 ms, respectively. SSLR INEPT is a superselective modification[5] of the known long-range INEPT (ref.[6]) technique based on the DANTE excitation of the chosen proton by a train of fractional soft pulses. The soft $\pi/2$ pulse used was 25 ms, the excitation train consisted of 1 000 25 μs fractional pulses separated by 50 μs delays; the evolution delays were varied according to the range of polarization transfer needed, their typical values being 12 and 6 ms.

RESULTS AND DISCUSSION

The ^1H and ^{13}C APT spectra of *II* are shown in Fig. 1. The numbering of signals of hydrogens and the carbons to which the hydrogens are bonded is the same. The compound *II* is assigned the structure as follows.

Proton signals 10 and 11 can be assigned by their shifts, splitting and strong cross-peaks in the COSY spectrum (Fig. 2). On the other hand, the assignment of 15 to carbonyl carbon is unequivocal in the ^{13}C spectrum. Proton signals 5 and 6 belong, according to their shifts, to an aromatic system; they are weakly coupled in COSY and they both transfer polarization to carbon 15 in SSLR INEPT (INEPT in the following). In the RCT spectrum (Fig. 3), which shows direct H–C correlations as well, they are correlated with the carbon signals 5 and 6, which are shown by APT to belong to aromatic CH carbons. In INEPT under longer evolution times, protons 5 and 6 transfer

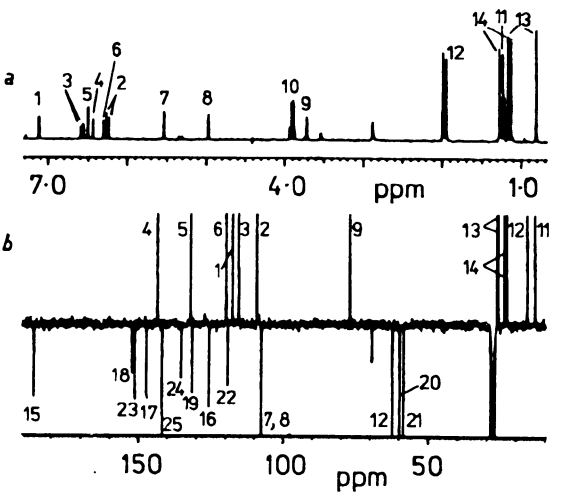


FIG. 1
^1H (*a*) and ^{13}C APT (*b*) spectra of *II* in $(CD_3)_2CO$ with HMDS as internal standard

polarization to carbons 18 and 16, respectively, and so do both of them to carbon 17. Signals 16, 17 and 18 are shown by APT to belong to aromatic quaternary carbons. It was found, in INEPT that carbon 16 receives polarization from methyl protons 12. These protons correlated with the methyl carbon in RCT, transfer polarization to carbon 19 (aromatic quaternary according to APT) and less easily to carbon 4 which is aromatic CH in APT and is correlated to aromatic proton 4 in RCT. Proton 4 has a weak cross-peak with protons 12 in COSY, indicating long-range coupling; in INEPT, it interacts with carbons 19 and 20. The latter is aliphatic quaternary according to APT, and receives polarization from the slightly nonequivalent methyl protons 13. All these facts lead to the conclusion that the investigated compound contains a quinoid quinoline moiety A (see formula *II*).

Another aliphatic quaternary carbon 21 interacts in INEPT with the pair of non-equivalent methyls 14 and with the isolated proton 9; the shift of the latter indicates α-position to a hydroxy group and so does the shift of the correlated carbon 9 (aliphatic CH carbon in APT). Proton 9 transfers polarization to the quaternary carbon 22 which also receives polarization from protons 7 and 8 in INEPT. Protons 7 and 8, though magnetically non-equivalent, are correlated in RCT to the same carbon which is shown by APT to be an unsaturated CH_2. In COSY, protons 7 and 8 show a weak cross-peak which indicates a slight geminal coupling. In INEPT, proton 8 transfers polarization to aromatic quaternary carbon 23 which shows a stronger interaction with aromatic proton 1. Proton 1 has a COSY cross-peak with proton 2 which is additionally coupled to proton 3 as well; the splitting of 1 indicates meta coupling, whereas that of 3 corre-

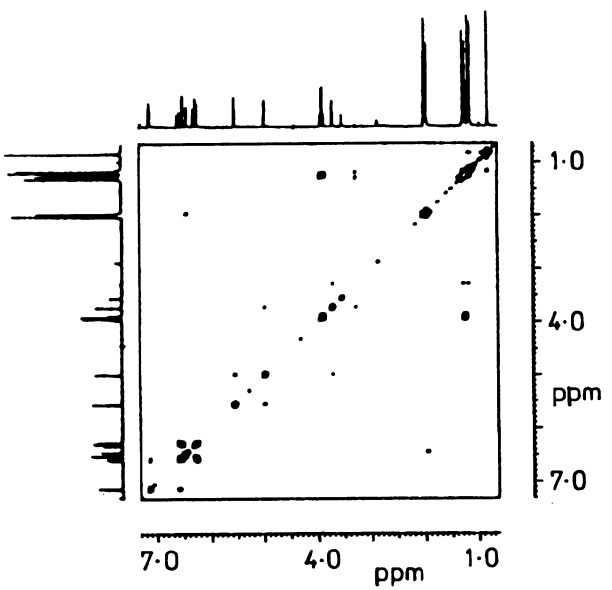


FIG. 2
^{1}H COSY spectrum of *II* in $(CD_3)_2CO$ with HMDS as internal standard

sponds rather to the ortho position. Protons 1 and 3 transfer polarization to aromatic quaternary carbon 25 whereas proton 2 interacts with the only remaining quaternary carbon 24. On the basis of these findings, the rest of the compound *II* is assigned the structure B.

Further evidence of the structure of *II* comes from the NOESY spectrum shown in Fig. 4. In addition to the unsufficiently suppressed *J* cross-peaks of the proton pairs 1-3,

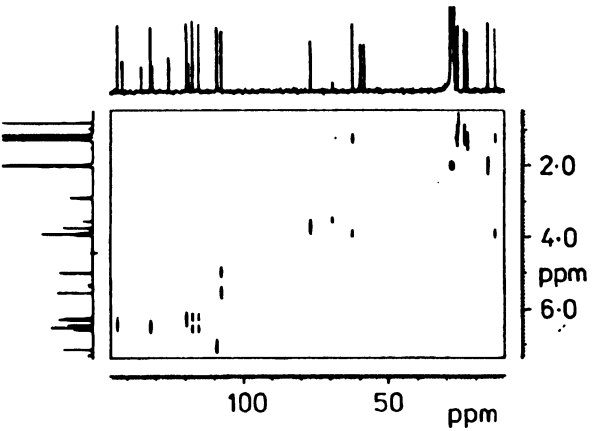


FIG. 3
^{1}H-^{1}H-^{13}C RCT spectrum of *II* in $(CD_3)_2CO$ with HMDS as internal standard

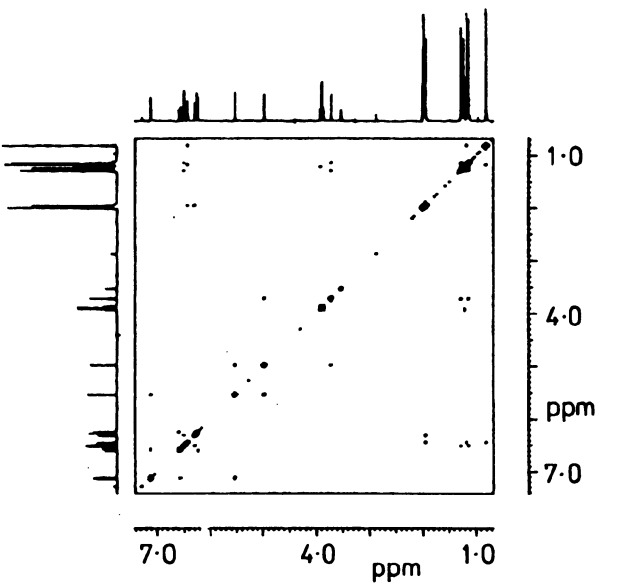
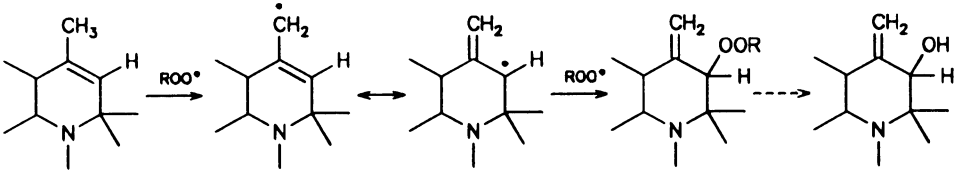


FIG. 4
^{1}H NOESY spectrum of *II* in $(CD_3)_2CO$ with HMDS as internal standard

5-6 and 7-8, the proximity of the proton pairs 5-14, 3-13, 6-12, 8-9, 1-7, and 9-14 is shown by the true NOE cross-peaks. The proximity of protons 5 and 14 or 3 and 13 indicates the linking of A to B.

In full agreement with the NMR findings, the high-resolution mass spectrum of *II* shows a high-intensity molecular peak with isotopic satellites confirming the expected formula $C_{26}H_{30}N_2O_3$ and the fragment $C_{25}H_{27}N_2O_3$ (M – CH_3); further characteristic fragments are $C_{14}H_{18}NO_2$ (B), $C_{12}H_{14}NO$ (AH_2), $C_{12}H_{13}NO$ (AH) and $C_{12}H_{12}NO$. Thus, the structure of *II* can be considered to be established.

Besides the N–H hydrogen abstraction, rearrangement and dimerization, a new mechanism of the reaction of ethoxyquin with peroxy radicals based on the elucidation of the structure of *II* can be suggested: The 4-methyl group of *I* or of some of its transformation products reacts with peroxy radicals, probably by the mechanism shown in Scheme 1.



SCHEME 1

Further confirmation of the new mechanism as well as the evaluation of its role in manifold reactions by which ethoxyquin deactivates peroxy radicals will be the subject of a separate paper[1].

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