BRIEF COMMUNICATIONS

A NEW QUINONE FROM *Salvia nemorosa*

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We have previously [1, 2] reported the isolation from the roots of Salvia nemorosa L. (violet sage) of the diterpene quinones acetoxyroyleanone $C_{22}H_{30}O_5$ (I) with mp 211.5-214° C and hydroxyroyleanone (horminone) $C_{20}H_{28}O_4$ (II) with mp 173-174° C.

By preparative chromatography on plates of silica gel G in the chloroform–ethyl acetate (85 : 15) system we obtained a yellow crystalline substance with the composition $C_{22}H_{28}O_6$, mp 192-194° C (decomp.; from ethanol), which proved to be new and which we have called nemorone (III). Nemorone has one acetoxy group (by the Kuhn-Roth method) and one mobile hydrogen (Tserevitinov [Zerewitinoff]). The IR spectrum of the substance (mull in paraffin oil), taken on a UR-10 spectrometer, showed absorption bands at (cm^{-1}) 3320, 1720 (strong), 1651, 1640, and 1620. In chloroform solution, the band at 1640 cm^{-1} underwent a shift in the high-frequency direction and became superposed on the band of the quinoid carbonyl at 1650 cm^{-1}, while the band at 3320 cm^{-1} (OH) shifted to 3430 cm^{-1}; consequently the band at 1640 cm^{-1} relates to a quinoid carbonyl linked by an intramolecular hydrogen bond with a neighboring hydroxy group. In chloroform, the 1720 cm^{-1} band is split into two, one of which is shifted to 1743 cm^{-1}, which is characteristic for carbonyl groups of esters; the second band is due to an aldehyde group.

The UV spectrum of nemorone, taken on a Hitachi EPS-3T spectrometer [λ_{max}^{EtOH} 266, 310 (inflection), and 410 nm (log ε 3.92, 3.13, and 2.95)] confirmed the presence of a hydroxy-p-benzoquinone grouping in this compound [3]. The molecular formula of $C_{22}H_{28}O_6$, the NMR spectrum characteristic of ferruginol derivatives [4], and its presence in the plant together with acetoxyroyleanone and hydroxyroyleonone (horminone), suggested a tricyclic diterpene skeleton for nemorone.

In the NMR spectra, taken on a Varian HA-100D spectrometer (100 MHz, $CDCl_3$) there were two singlets (each with an intensity of 3H) of gem-dimethyl groups at 0.94 ppm (C_4-CH_3^e) and 0.77 ppm (C_4-CH_3^a), which is explained by the diamagnetic influence of the aldehyde group at C_{10}, the signal of the proton of which is located at 10.10 ppm. The methine proton of the isopropyl group of ring C gives a signal in the form of a septet at 3.18 ppm, and the signals of its methyl groups (two doublets of 3H each at 1.18 and 1.26 ppm; J = 7 Hz) were split, which is the case in compounds with a hydroxy group at C_{12} and an acetoxy group in ring B. The singlet (1H) at 6.90 ppm relates to the C_{12}-OH group and the singlet (3H) at 2.06 ppm to the C_7-$OCOCH_3$ group. The equatorial gem-acetyl proton at C_7 gives a signal at 5.99 ppm ($\Delta W_{1/2}$ = 8 Hz), which shows the α-axial orientation of the C_7 acetoxy group [5].

In the NMR spectrum of the compounds $C_{20}H_{26}O_5$ (M^+ 346) (IV) obtained by the alkaline hydrolysis of nemorone, the signal of the methyl of the acetoxy group at 2.06 ppm has disappeared. Furthermore, on passing from nemorone to its hydroxy analog, as was to be expected, the signal of the equatorial proton at C_7 has shifted upfield by 1.17 ppm.

In a study of the mass spectra of substances (I-IV) using a MKh-1303 mass spectrometer, it was found that the acetyl group is responsible for a very low intensity of the molecular peak. It was also found that in the mass spectra of acetoxyroyleanone and nemorone the first strong peaks in the region of large masses appear as the result of the splitting out of an isopropyl group with the transfer of its methine hydrogen to C_{13} ($M^+ - C_3H_6$), while in the mass spectrum of hydroxyroyleanone and the hydrolysis product

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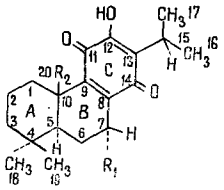
of nemorone the peak with m/e 317 following the strong molecular peaks (M^+ 332 and 346, respectively) is due to the detachment of a methyl group in the first case and of an aldehyde group in the second case from C_{10}.

Thus, the quinone with the composition $C_{22}H_{28}O_6$ isolated from the roots of the violet sage and called nemorone has the structure 7-acetoxy-10-formyl-12-hydroxy-13-isopropyl-4,4-dimethyloctahydrophenanthrene-11,14-quinone.



I $R_1 = OCOCH_3$; $R_2 = CH_3$
II $R_1 = OH$; $R_2 = CH_3$
III $R_1 = OCOCH_3$; $R_2 = CHO$
IV $R_1 = OH$; $R_2 = CHO$

LITERATURE CITED

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