

Table 1. Atomic coordinates and thermal parameters of Rh₇Mg₄₄.

Atom	Special positions	x	z	B (Å ²)
Rh(1)	in 24 g	1/4	0.5867 ± 1	1.03 ± 4
Rh(2)	in 16 e	0.0833 ± 1		0.70 ± 4
Rh(3)	in 16 e	0.3488 ± 1		0.68 ± 4
Mg(1)	in 48 h	0.0525 ± 3	0.3380 ± 4	1.1 ± 1
Mg(2)	in 48 h	0.1072 ± 3	0.2141 ± 4	1.0 ± 1
Mg(3)	in 48 h	0.1949 ± 3	0.4806 ± 4	0.7 ± 2
Mg(4)	in 48 h	0.0961 ± 3	0.7206 ± 5	1.4 ± 1
Mg(5)	in 48 h	0.1565 ± 3	0.9795 ± 4	1.0 ± 1
Mg(6)	in 24 g	1/4	0.3553 ± 6	0.9 ± 1
Mg(7)	in 24 f	0	0.1824 ± 7	1.2 ± 2
Mg(8)	in 16 e	0.6956 ± 4		0.7 ± 2
Mg(9)	in 16 e	0.8338 ± 4		0.5 ± 2
Mg(10)	in 16 e	0.5618 ± 6		1.8 ± 3
Mg(11)	in 16 e	0.9476 ± 4		0.9 ± 2

metal-magnesium contact found in Pd₂Mg₅, viz. 2.59 Å.⁶ A detailed description of this structure will be published subsequently.

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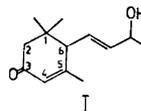
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Tobacco Chemistry 7. Structure and Synthesis of 3-Oxo- α -ionol, a New Tobacco Constituent

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During the chemical study of the volatile constituents of sun-cured Greek tobacco, *N. tabacum* grown in Serres 1968, we have isolated a new compound (14 ppm of dry tobacco) which has been assigned structure I on the basis of evidence presented below and is now named 3-oxo- α -ionol.



Accurate mass measurements suggested that I had the composition C₁₃H₂₀O₂. (Found 208.1457, calc. 208.1463.) The UV spectrum in ethanol exhibited a maximum at 235 nm (ϵ 9000) indicating the presence of a disubstituted conjugated ketone grouping. This assignment was supported by a band at 1657 cm⁻¹ in the IR spectrum (film) which also displayed diagnostically important bands at 3400 cm⁻¹ (hydroxyl), 1369 cm⁻¹ and 1376 cm⁻¹ (*gem.* dimethyl) and 976 cm⁻¹ (*trans* disubstituted double bond). The NMR results (60 MHz, CDCl₃, TMS) are summarised in Table 1.

Decoupling experiments revealed that the protons resonating at 1.91 and 5.96 ppm are coupled (J 1.4 Hz), consistent with the presence of a -CO-CH=C(CH₃)- group. The protons giving rise to the signals at ca. 4.4 and 1.31 ppm were similarly shown to be coupled (J 6.3 Hz) to each other and can readily be associated with

a -C=C-CH(OH)-CH₃ moiety. The broad signal at 2.4 ppm disappeared on addition of D₂O and was thus due to a hydroxyl proton. The broad singlets at 2.17 ppm (ca. 1H) and 2.26 ppm (ca. 1H) seem to form the inner lines of an AB-

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Table 1. Significant data and assignments from the NMR spectrum of 3-oxo- α -ionol.

Chemical shifts ppm	Number of protons	Signal pattern	Assignment
5.96	1	broad singlet	$-\text{CO}-\text{CH}=\text{C} <$
ca. 5.7	2	multiplet	$-\text{CH}=\text{CH}-$
ca. 4.4	1	broad quartet	$-\text{CH}(\text{OH})-\text{CH}_3$
ca. 2.6	1	multiplet	$> \text{CH}-$
ca. 2.4	1	broad singlet	$-\text{OH}$
2.26	1 (ca.)	broad singlet	$-\text{CO}-\text{CH}_2-$
2.17	1 (ca.)	broad singlet	
1.91	3	doublet, J 1.4 Hz	$-\text{CH}=\overset{\text{O}}{\text{C}}-\text{CH}_3$
1.31	3	doublet, J 6.3 Hz	$-\text{CH}(\text{OH})-\text{CH}_3$
1.04	3	singlet	$> \text{C}(\text{CH}_3)_2$
0.99	3	singlet	

⁸ system and may be ascribed to a methylene group adjacent to a carbonyl. The mass spectrum of I displayed significant peaks at m/e 208, 193, 190, 175, 165, 152, 134, 108 (100%), 95, 91, 79, 77, 45, 43, and 41, the intensities of which (except for the m/e 108 ion) were all below 30%. The m/e 152 and 134 peaks correspond with losses of isobutene and isobutene plus water consistent¹ with the suggested structure.

Oxidation of I gave a diketone which did not show a bathochromic shift in the ultraviolet relative to the parent compound but rather displayed an enhanced absorption at slightly shorter wavelength suggesting the introduction of a second chromophore such as a monosubstituted α,β -unsaturated ketone. The NMR spectrum was compatible with this and revealed that the two olefinic protons giving rise to signals at 6.18 and 6.72 ppm, respectively, were in a *trans* relationship to each other (J 15.5 Hz).

Acetylation of I furnished a monoacetate, the NMR spectrum of which displayed an 'acylation shift'² of ca. 1.1 ppm confirming the presence of a secondary hydroxyl.

Based on the information given above, and using isophorone, α - and β -ionone, and α - and β -ionol as model compounds for the interpretation of the NMR spectrum, structure I appeared probable. Conclusive evidence was obtained by comparison of synthetic *trans*-(\pm)-3-oxo- α -ionone³ and *trans*-(\pm)-3-oxo- α -ionyl-

acetate with the corresponding derivatives of the natural compound on the basis of their identical NMR, IR, and mass spectra. The syntheses were effected by allylic oxidation of *trans*-(\pm)- α -ionone and *trans*-(\pm)- α -ionylacetate with chromic acid in acetic acid.⁴ The NMR, IR, and mass spectra of *trans*-(\pm)-3-oxo- α -ionol obtained by saponification of the synthetic acetate were found to be identical to those of the natural compound, thus confirming the *trans* configuration of the double bond.

Work is in progress to elucidate the stereochemistry at the two asymmetric carbon atoms of I since this compound is optically active ($[\alpha]_D^{20} + 177^\circ$, c 1.0, ethanol). A full account of these results will shortly be presented.

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