Structure and Autoxidation of Atractylon

The crystalline sesquiterpenoid, atractylon, was first isolated from the crude drug "Sō-jutsu" and later from *Atractylodes japonica* Koidzumi and its related plant. The present communication contains evidence which permits the assignment of expression (I) to atractylon and expressions (IV) and (V) to its autoxidation products.

Atractylon (I), C_{15}H_{20}O, m.p. 38°, \([\alpha]_D^0 +40.0°\), had infrared spectrum which exhibited no band associated with hydroxyl or carbonyl grouping but a band at 1134 cm\(^{-1}\) assigned to ether mode. The presence of the furan system in (I) was indicated from the positive color reactions for furan ring such as vanillin-HCl, pine stick, Ehrlich, Liebermann–Burchard reactions and from ultraviolet spectrum (\(\lambda_{\text{max}}^\text{EtOH} 220\) mμ) as well as from the formation of maleic anhydride adduct, C_{19}H_{22}O_4, m.p. 118°. The third ethylenic bond as in exocyclic was revealed by infrared absorption (bands at 3077, 1639, 886 cm\(^{-1}\)) and by ozonolysis to give formaldehyde. Catalytic hydrogenation of (I) over PtO\(_2\) in MeOH resulted in the saturation of the exocyclic double bond to afford the dihydron derivative (II), C_{15}H_{22}O, b.p. 101°, \([\alpha]_D^0 -44.0°\). The retention of the furan system in (II) was indicated by the coloration given with reagents described above and by UV: \(\lambda_{\text{max}}^\text{EtOH} 221\) mμ. On catalytic hydrogenation in AcOEt using Pd-C, (I) took up three moles of H\(_2\) with the formation of a saturated oxide (III), C_{15}H_{26}O, b.p. 120-122°, \([\alpha]_D^0 -51.4°\), which was identified (IR spectra) with octahydrodesoxylenderene. In agreement with the proposed structure, nuclear magnetic resonance spectrum of (I), measured at 40 Mc. in CCl\(_4\) vs. H\(_2\)O as external reference, showed the following peaks: singlet (3H) at +160 c.p.s., doublet (3H) at +114 c.p.s. (J 1 c.p.s.), doublet (2H) at +1 c.p.s. (J 5 c.p.s) with additional fine splitting, unresolved band (1H) at -87 c.p.s.

\[\text{O}\]
\[\text{H} (\text{I}) \quad \text{H} (\text{II})\]
\[\text{O} \quad \text{H}\]
\[\text{CO}\]
\[\text{OH}\]
\[\text{CO}\]
\[\text{OH}\]
\[\text{CO}\]
\[\text{H}\]
\[\text{CO}\]
\[\text{H}\]
\[\text{N-C}_5H_5\]

\(*1\) All analytical values are in good agreement with the molecular formula shown. \([\alpha]_D^0\)s refer to CHCl\(_3\) solutions.

(I) suffered remarkably rapid autooxidation on standing in air to give two crystalline products, (IV), C₁₅H₂₀O₂, m.p. 125°, [α]₀ +266.1°, and (V), C₁₅H₂₀O₃, m.p. 197~197.5°, [α]₀ +281.4°. The presence of a α,β-butenolide system in both (IV) and (V), was confirmed by the spectral properties in ultraviolet (λmax 220 μm) and infrared region (bands at 1733, 1672 and 1736, 1695 cm⁻¹, respectively). (IV) and (V) showed also infrared bands at 900 and 897 cm⁻¹ (vinylidene) and yielded formaldehyde on ozonolysis. On hydrogenation with Pd-C in AcO Me, (IV) and (V) gave dihydro-derivatives, (VI), C₁₅H₂₂O₂, m.p. 114~115°, [α]₀ +130.8°, and (VII), C₁₅H₂₂O₃, m.p. 178~179.5°, [α]₀ +299.0°, respectively, which retained the spectral properties due to α,β-butenolide but disclosed no >C=CH₂ absorption. That the last oxygen in (V) was the hydroxyl group situated as hemiketal lactone form in the α,β-butenolide system was established from the following observations: (V), UV: λmax OH-EtOH 264 μm, IR: νNujol 3333 cm⁻¹, exhibited the weakly acidic properties, reacted with phenylhydrazine to give a product (VIII), C₁₇H₂₄ON₂, m.p. 210~212°, and was easily dehydrated to afford an anhydroderivative (IX), C₁₃H₁₈O₂, m.p. 106~108°, UV: λmax 275 μm, from which (V) was regenerated by dissolution in alkali followed by acidification. Hydrogenation of (V) over PtO₂ in AcOH in the presence of HCl led to a saturated lactone (X), C₁₃H₂₄O₂, m.p. 141~143°, [α]₀ +15.2°, which was identified (m.p., mixed m.p. and IR spectra) with tetrahydroalantolactone. It is very probable that (IV) is the desoxy-compound of (V). (VI) was proved to be identical (m.p., mixed m.p. and IR spectra) with the butenolide⁵ derived from alantolactone. Although the autooxidation process from (I) to (V) has a few examples,⁶ that from (I) to (IV) seems to have no precedence.

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