A Novel Rearrangement of an Analogue of Humulone

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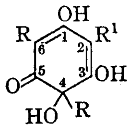
ONE of the characteristic features of humulone (I) is its readiness to undergo a ring contraction in alkaline media to form *cis*- and *trans*-forms of isohumulone (II) or humulinic acid (III).[1] A similar type of rearrangement can occur in acidic media but many by-products of unknown structure are then also formed.

The products formed by heating an analogue (IV) of humulone under reflux in aqueous alkaline and acidic media have now been investigated. The compound (V) is formed under a wide variety of pH conditions and is the major product when (IV) is refluxed with 2N-hydrochloric acid for 2 hr. The u.v. spectra of (V), λ_{max} 272 mμ (in alkaline ethanol), 250 mμ (in acidic ethanol) are in agreement with this structure and the i.r. spectrum (ν_{max} 1710, 1630, 3400 cm.$^{-1}$) is typical of a β-diketone system. The mass spectrum gives a molecular ion at 198 (5%) and a base peak at 142. The n.m.r. spectrum indicates an absence of both acetyl and olefinic protons and shows two overlapping triplets (τ 8·98, 3H, J 6; τ 8·84, 3H, J 6 c./sec.) assignable to the side-chain methyl groups and two quartets (τ 7·52, 2H, J 6; τ 7·04, 2H, J 6 c./sec.) corresponding to the side-chain methylene groups. A partially obscured AB quartet centred at about 6·84 (J 17 c./sec.), corresponding in intensity to approximately two protons, can be assigned to the C-2 methylene group.

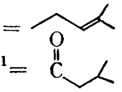
Compound (V) formed (a) a diacetate with acetic anhydride in pyridine, (b) a monomethyl ether with diazomethane, and (c) a trimethylsilyl derivative with hexamethyldisilazane in dimethyl formamide. The molecular weights of these derivatives have been confirmed by mass spectrometry. All the above derivatives are suitable for examination by g.l.c. but chromatography of the underivatised (V) results in extensive deacylation to yield (VII). Treatment of (V) with chromium trioxide in acetone yielded, amongst other unidentified products, 5-ethylcyclopenta-1,3,4-trione.

Treatment of the corresponding analogue (VI) of isohumulone with 2N-hydrochloric acid did not give (V); therefore deacylation of (IV) probably occurs prior to the ring contraction. A ring contraction leaving an acyl side-chain at C-**3** rather than at C-4 has not previously been established in the chemistry of the hop constituents.



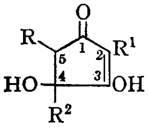
(I) R=

R1=



(IV) R=Et

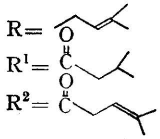
R1=Ac



(II) R=

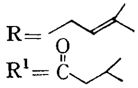
R1=

R2=



(III) R=

R1=

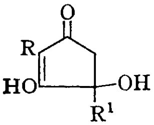


R2=H

(VI) R=Et

R1=Ac

R2=COEt



(V) R=Et, R1=COEt

(VII) R=Et, R1=H

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[1] R. Stevens, *Chem. Rev.* 1967, **67**, 19.