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TRICYCLODEHYDROISOHUMULONE

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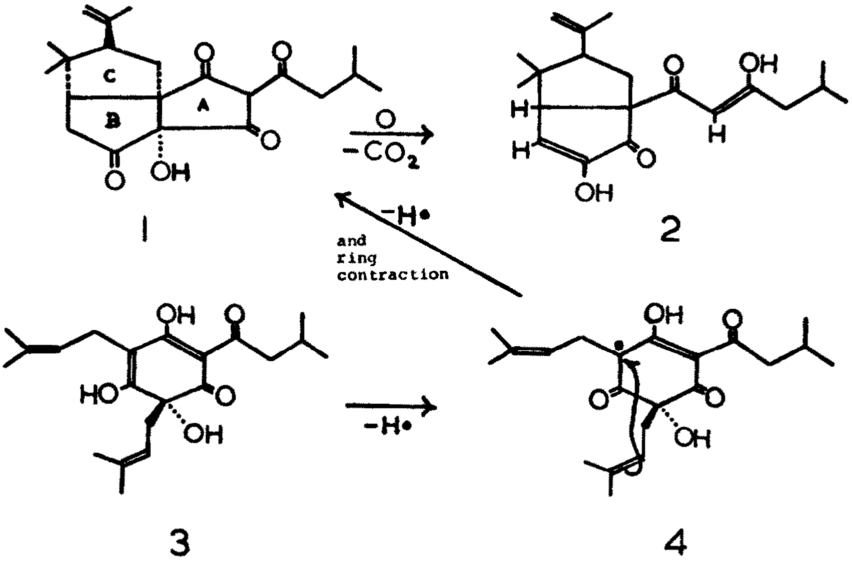
Tricyclodehydroisohumulone, $C_{21}H_{28}O_5$, a new bittering component detected in beer and stored hops, was assigned a fused 5,5,6-tricyclic structure on preliminary chemical and spectroscopic evidence.[1] We now report a revision to the fused 5,5,5-tricyclic structure (1), resulting from further degradative work.

The previously presented results accord with either structure. The new definitive evidence for (1) comes from degradation with periodate[2] which yields the product (2). Thus tricyclodehydroisohumulone was oxidised in dilute solution (1:1 aq. dioxan) with sodium metaperiodate at 20°C for 2 weeks. The solution was diluted and extracted with ether, the extract was chromatographed (ethyl acetate-petroleum ether) on silicic acid, and the required component isolated with ether. Its composition, $C_{20}H_{28}O_4$ ($\underline{M}^+$ 332·1986), corresponds to oxidative cleavage of ring A in (1) with loss of one carbonyl group as carbon dioxide. Further evidence for retention of the acyl side chain in the form of an enolised β-dicarbonyl substituent is provided by the strong u.v. absorption (in EtOH) at 272 nm[3] and loss on electron impact of C_5H_9O and then C_2H_2O fragments (m/e 247.1334 and 205). These findings and the intense i.r. absorption at 1702 cm^{-1}[4] indicate the 5-membered ring diosphenol structure (2) for the degradation product, which is fully supported by the CH resonances in the ^1H n.m.r. spectrum; $\tau(CDCl_3)$ 9.43 (3H,s), 8.82 (3H,s), 9.09 (6H, d, $\underline{J}$ 7 Hz), 8.31 (3H,s), 8.14 - 7.36 (6H,c), 5.43 and 5.17 (2H), 4.48 (1H), 6.66 and 3.44 (each 1H, d, $\underline{J}$ 3.3 Hz). The structure (2) for the degradation product taken together with previous evidence leads unambiguously to (1) for tricyclodehydroisohumulone.

Tricyclodehydroisohumulone (1) appears to arise by slow aerial oxidation of humulone(3) in stored hops ; it is obtainable in 30% yield by oxidation of humulone with lead tetraacetate.[1] The primary act is probably formation of the radical (4) which then cyclises as indicated to a bicyclic radical species which through ring contraction (as in isomerisation of humulone to isohumulone)[5] and oxidative coupling of the α-orientated side chains would lead to (1) with the configuration shown. If the last two steps occurred in reverse order, the orientation of the isopropenyl group in (1) would be uncertain.

The structure (1) is completely novel amongst hop resin constituents and their transformation products.



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