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THE STEREOCHEMISTRY OF 2-HYDROXYPINOCAMPHONE

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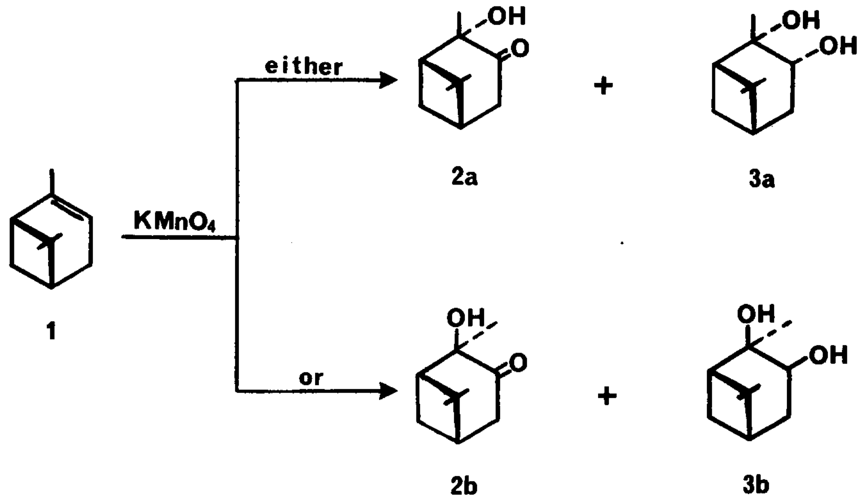
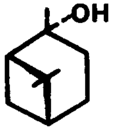
Several groups of workers have examined the oxidation of α-pinene (**1**) with potassium permanganate[1-5] and there is general agreement that this oxidation produces a cis-glycol and a ketol, 2-hydroxypinocamphone. There is, however, no general agreement as to the stereochemistry of these products. Schmidt[3] originally assigned configurations **2a** and **3a** to the ketol and cis-glycol, respectively, but later[6] changed his assignment to **2b** and **3b** based on the products of rearrangement reactions. More recently[7] chemical evidence in favor of **2a** and **3a** has been presented, while some of us[4] have interpreted spectral data and the ORD and CD curves of **2** as requiring configurations **2b** and **3b** for these products. The correct stereochemical assignment to these products is of utmost importance because if **2b** and **3b** are correct representations of these compounds this requires that permanganate attack the double bond of α-pinene from the same side as the gem-dimethyl bridge. It has been generally assumed that the attack of external reagents on the pinane skeleton will occur from the side opposite the gem-dimethyl

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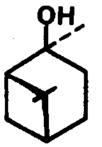
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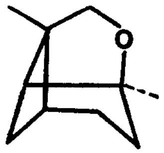
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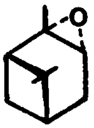
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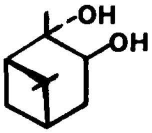
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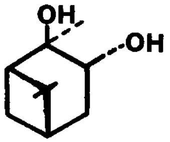
8b

bridge and this assumption has been used in stereochemical assignments to the vast majority of pinane derivatives.[8] Thus, if 2b and 3b represent the correct stereochemistry of these products a complete re-examination of the stereochemistry of the pinane derivatives is in order.

We wish to provide what we feel is compelling chemical evidence in favor of 2a and 3a for the products of permanganate oxidation of α-pinene. We will assume for the moment that the recent spectral data[4] are correct and not rely on chemical correlation with any compounds whose stereochemistry has been assigned on the basis of attack of external reagents from the least hindered side. Fortunately, there is one pair of isomeric compounds, *cis*-2-pinanol(4) and *trans*-2-pinanol(5), for which unambiguous chemical proof of stereochemistry is available. A recent study has shown that treatment of 5 with iodine and lead tetraacetate or bromine and mercuric oxide leads to the bridged ether 6 in 85-90% yield.[9] This clearly and unambiguously establishes the stereochemistry of this pair of compounds. The accompanying communications describing the rearrangement of the monotosylates of the *cis*- and *trans*-glycols derived from 2 provide a correlation between 2 and 4 and 5.

Base treatment of the monotosylate of the *trans*-diol (8a or 8b) obtained by metal hydride reduction of 2 leads to an α-pinene oxide which is identical in all respects with the α-pinene oxide obtained by peracid epoxidation of α-pinene and which has an ir spectrum identical with that published by Huckel,[10] who carefully established the stereochemical homogeneity of this α-pinene oxide. Reduction of this α-pinene oxide with Na-K in moist ether gave, among other products, *cis*-2-pinanol(4) and none of 5 could be detected among the products.[10] Thus, α-pinene oxide must have structure 7. Because the nmr data on the monotosylate of *trans*-diol derived from 2 clearly indicates that the secondary hydroxyl group was esterified and because inversion at C-2 is extremely unlikely in the epoxide formation from the monotosylate it follows that the *trans*-diol derived from 2 must have structure 8a and therefore 2a and 3a represent the correct stereochemistry of products obtained on permanganate oxidation of α-pinene.[11]

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