

**SPIROS ARE EVERYWHERE.**

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**ABSTRACT:** Dihydroxyketones (ketodiols), bearing the two hydroxy groups on either side of the carbonyl group may form bicyclic products (spiroacetals = spiroketals - see sketch: X and Y = 1,2, or 3) upon intramolecular cyclisation. So far, five different systems have been found in nature: compounds showing two 5- to 7-membered rings and mixed structures. In two cases, spiros carry a double bond in one of the rings. Apart of very few exceptions, the carbon skeletons of these volatiles are unbranched, indicating an origin from the acetate pool. Because of the anomeric effect, caused by the two oxygens adjacent to the spiro center, the thermodynamical stability of the possible diastereomers is different, and therefore, the natural products may show very different proportions. Compound A (see sketch) usually co-occurs with B, C, and D, however, amounts of D do not exceed 1-2% of that of A. In contrast, E and F, which may be associated with A-D, usually occur in a relation of about 1:1. Reasons will be discussed. It should be noted that the natural mixtures do not show the thermodynamically most stable composition of stereoisomers. For structure elucidation of natural spiros, it is important to understand the principles of their mass spectrometric fragmentation.

Showing a multitude of biological activities, spiros are widespread in nature and have been found in microorganisms, plants (flower volatiles), and animals (insects, mammals).

