Pheromones: Identification and Synthesis of Bicyclic Acetals

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Bicyclic acetals formed from cryptic ketodiols play a major role as intraspecific and interspecific chemical signals. According to their chemical structures, they are generally represented by alkylated 2,7-dioxabicyclo[2.2.1]heptanes (**1**), 2,8-dioxabicyclo[3.2.1]octanes (**2**), 6,8-dioxabicyclo[3.2.1]octanes (**3**-**6**), 2,9-dioxabicyclo[3.3.1]nonanes (**7**), and spiroacetals showing various ring sizes (**8**-**12**).

General aspects on the mass spectrometric fragmentation pattern of these compounds will be discussed. This may facilitate identification of trace amounts of biologically active components in complex mixtures. Structure elucidation and synthesis of some new bicyclic acetals will be presented: (**1**) has been found in ants and man; hydroxylated derivatives of brevicomin (**3**) and frontalin (**4**) are produced by some *Dendroctonus* bark beetles; (**5**) is the aggregation pheromone of the beech bark beetle, *Taphororychus bicolor*; (**7**) and its 6-oxo derivative are part of the male pheromone of the swift moth, *Hepialus hecta*. The spiroacetals (**9**) and (**10**) are components of the bouquet of the Mediterranean almond bark beetle, *Scolyfus mediterraneus* – the typical *Scolytus* pheromone being multistriatin (**6**). The widespread spiroacetal (**11**) and its homologue (**12**) are main components in the defensive secretion of the shield bug *Canto parentum*.

Brevicomin (**3**) and the spiroacetals (**8**-**11**) represent acetogenins. The structures of some spiroacetals are closely related to indolizidines and pyrroloindolizidines which are known as ant toxins. While the biosyntheses of (**1**), (**4**), and possibly (**5**) appear to involve isoprenoids, (**2**), (**6**), and (**7**) seem to originate from mixed sequences involving acetate – and propanoate-units.

The non-natural 1-methyl-2,10-dioxabicyclo[4.3.1]decane (**13**) rearranges under relatively mild conditions to either (**9**) or to the tetrahydrofuran (**14**). Whether similar processes are also occurring under physiological conditions is yet unknown.