"Junionone" [1-(2,2-Dimethylcyclobutyl)but-1-en-3-one], the first Vegetable Monocyclic Cyclobutane Monoterpenoid

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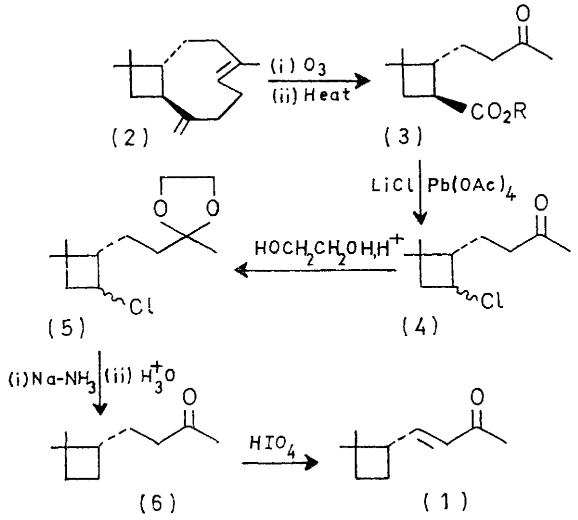
Summary "Junionone" [1-(2,2-dimethylcyclobutyl)but-1-en-3-one], the first vegetable monocyclic cyclobutane monoterpenoid, has been isolated from the oil of the fruit of *Juniperus communis,* L.

IN the course of an analysis of the oil of the fruit of *Juniperus communis,* L.,[1] we isolated[†] a substance, $C_{10}H_{16}O$ (confirmed by mass spectrum) with an n.m.r. spectrum indicative of the group MeCOCH=CH–CH [Me group at δ 2·26, vinyl protons at 6·0 (doublet) and 6·87 (doublet of doublets), CH at 2·71], together with two further methyl groups (1·02 and 1·13). Addition of the shift reagent, $Eu(fod)_3$,[2] showed that the remaining two methylene groups were not identical, so there was a strong indication that the compound was 1-(2,2-dimethylcyclobutyl)-but-1-en-3-one (**1**). Formula (**1**) is drawn to correspond with the substance ($[\alpha]^{20}_{D}$ $-9°$) obtained from caryophyllene; insufficient natural material was available to be certain about its optical activity.



Compound (**1**) was prepared from caryophyllene (**2**) by ozonolysis to the known acid (**3**; R = H), isolated as its methyl ester (**3**; R = Me),[3] followed by decarboxylation[4] with lead tetra-acetate and lithium chloride to a mixture of the two stereoisomeric chlorides (**4**). These were reduced in the form of the acetals (**5**) with sodium in liquid ammonia, when deacetalization gave the saturated cyclobutyl ketone (**6**). The double bond was introduced with periodic acid in 50% aqueous dioxan in poor yield,[‡] and the product (**1**) was identical in retention time on two different columns, and by n.m.r., mass, i.r., and u.v. spectra with the natural product.

This new monoterpenoid, for which we suggest the name junionone, can clearly arise by fission of a bond of the pinane skeleton, and is thus not a regularly head-to-tail linked isoprenoid. Although a monocyclic cyclobutane monoterpenoid has been isolated from an animal source,[5] this is the first report of such a system in a plant.

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[†] The isolation method involved a combination of distillation, column chromatography, counter-current distribution, and gas chromatography, and will be described in full later.

[‡] It is not generally realized that periodic acid reacts with saturated ketones. Iodinated products are obtained, and work-up by chromatography on silica gel and gas chromatography always yields the $\alpha\beta$-unsaturated ketone, though frequently in low yield. We intend to describe this reaction more fully elsewhere. Conversion of the saturated (**6**) into the unsaturated ketone (**1**) was also effected by bromination followed by dehydrobromination with lithium carbonate in dimethylformamide.

[1] For earlier reports on this analysis see A. F. Thomas, *Helv. Chim. Acta,* 1972, **55**, 815, 2429; 1973, **55**, 1800.

[2] R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.,* 1971, **93**, 1522.

[3] L. Ruzicka and A. H. Wind, *Helv. Chim. Acta,* 1931, **14**, 410.

[4] J. K. Kochi, *J. Amer. Chem. Soc.,* 1965, **87**, 2500.

[5] J. H. Tumlinson, D. D. Hardee, R. C. Gueldner, A. C. Thompson, P. A. Hedin, and P. Minyard, *Science,* 1969, **166**, 1010.