inhibition of NOA formation only occurs at ascorbic acid concentrations 2 or more times higher than the nitrite concentration i.e. in quantities 4 times the stoichiometric ones (reaction 2). Tannenbaum et al.[23] have also observed that some of the nitrite may not necessarily be active as nitrosating agent. A possible explanation may be associated, in analogy with the observed catalytic influence of phenols on dimethylamine nitrosation[22], with the formation, in a preequilibrium step, of the intermediate ascorbyl nitrite[13] as an 'activated' nitrosating agent. Such a species, although easily hydrolysed by acid, might survive sufficiently long to carry out nitrosations even in the presence of efficient inorganic nitrite scavengers. Until more evidence is available on this point it is therefore our opinion that even 'ascorbate protected' foodstuffs be more widely monitored for as yet undetermined NOAs possibly arising via this hitherto seldom considered route.

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The syntheses of spin labelled juvenoids

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Summary. 5 juvenoids labelled with stable nitroxyl radicals were synthesized and were shown to have morphogenetic effect on *Tenebrio molitor* L. and *Dysdercus cingulatus*.

Juvenoids labelled with tritium or ^{14}C are frequently used in studies of interactions of juvenile hormones and their analogs with biological receptors[1]. Spin labelled juvenoids have not yet been used in such studies and have never been described so far. In this communication we describe the preparation of juvenoids labelled with stable nitroxyl radicals to be used in biochemical studies. The synthetic routes which we followed in our syntheses are shown in the figure.

The syntheses started with readily available substrates such as geranylacetone (**1**), farnesol (**7**), and geraniol (**11**). A xylene solution of geranylacetone was refluxed in a Dean-Stark apparatus with 2-amino-2-methylpropan-1-ol in the presence of a catalytic amount of p-toluenosulfonic acid[2] to give 70% of oxazolidine **2**.

The oxazolidine **2** was next oxidized with m-chloroperbenzoic acid in diethylether to afford the nitroxyl derivative **3**; b.p. 180 °C/4 mm Hg[3], IR (film): 1375 cm^{-1}, 1250 cm^{-1}, 1160 cm^{-1}, 1118 cm^{-1}, EPR g-radical, $2\Delta B_{1S} = 1.37 \pm 0.01$ mT.

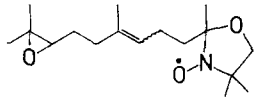
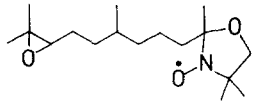
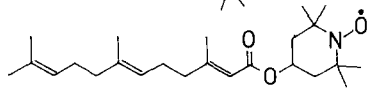
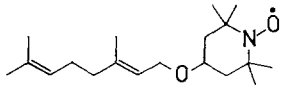
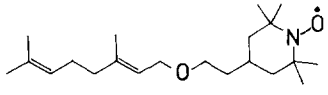
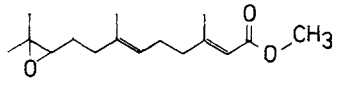
The dihydroderivative **6** was obtained in the same manner starting with dihydrogeranylacetone with overall yield 60%; b.p. 175 °C/2 mm Hg[3], IR (film): 1363 cm^{-1}, 1250 cm^{-1}, 1162 cm^{-1}, 1118 cm^{-1}, EPR g-radical, $a = 1.15 \pm 0.01$ mT, $2\Delta B_{1S} = 0.56 \pm 0.01$ mT. The nitroxyls **3** and **6** were obtained as stereoisomeric mixtures because the geranylacetone we used was a mixture of 2 isomers E/Z on double bond $C_5{=}C_6$ (65% E, 35% Z) and, moreover, the reactions with 2-amino-2-methylpropan-1-ol and m-chloroperbenzoic acid produced 2 racemic chiral centers at C-2 and C-9. A mixture of 4 isomers would be expected, but GLC analysis showed the presence of only 2. Since it was not possible to obtain any good NMR-spectrum (the presence in the molecule of an unpaired electron) we could not determine, at this stage of study, which stereoisomers were formed.

The compound **10**: b.p. 210 °C/3 mm Hg[3], IR (film): 1648 cm^{-1}, 1375 cm^{-1}, 1365 cm^{-1}, 1160 cm^{-1}, 1140 cm^{-1}, 890 cm^{-1}, EPR g-radical, $a = 1.57 \pm 0.01$ mT, $2\Delta B_{1S} = 0.41 \pm 0.01$ mT, was prepared by standard methods from commercial farnesol (Fluka). The ratio of $C_2{=}C_3$ double bond geometrical isomers was determine by GLC as 75% E and 25% Z.

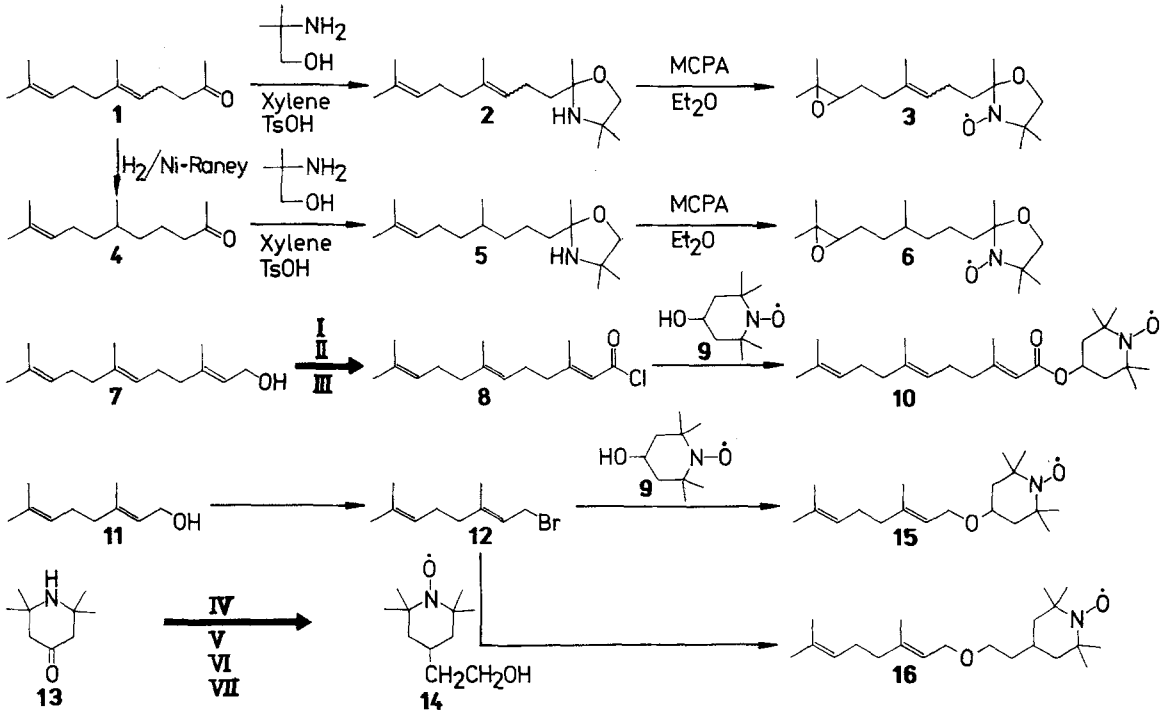
The syntheses of ethers **15** and **16** were carried out starting with geranyl bromide and appropriate spin labelled alcohols **9** and **14** using a method similar to that described by Nilles et al.[4] followed by purification by TLC on silicagel. Compound **15**: decomposed during distillation at 210 °C, IR (film): 1670 cm^{-1}, 1375 cm^{-1}, 1362 cm^{-1}, 1175 cm^{-1}, 1075 cm^{-1}, 785 cm^{-1}, EPR g-radical, $2\Delta B_{1S} = 2.4 \pm 0.02$ mT; compound **16**: decomposed during distillation at 220 °C, IR (film): 1665 cm^{-1}, 1375 cm^{-1}, 1362 cm^{-1}, 1175 cm^{-1}, 1105 cm^{-1}, 840 cm^{-1}; EPR g-radical, $2\Delta B_{1S} = 1.12 \pm 0.02$ mT.

Preliminary biological tests of spin labelled compounds **3**, **6**, **10**, **15** and **16** (*Tenebrio molitor* L., *Dysdercus cingulatus* L.) revealed that the highest JH-activity was exhibited by the nitroxyls **3** and **6**. Geranyl ether **16** has only weak activity and **15** is not active (table). The details of these investigations will be published in a separate paper.

Structure and JH activity of investigated compounds

Number	Structure	*T. molitor* L.[a] µg/specimen	*D. cingulatus* L.[a] µg/specimen
3		8	8
6		0.8	8
10		*Δ*[b]	8
15		*Δ*	*Δ*
16		*Δ*	80
JH-3		10	1

[a] ID_{50}; [b] *Δ*-Compound not exhibiting juvenile activity at the doses applied: ≲ 80 µg/specimen.



I MnO_2 (Corey and Gilman[5]). **II** Ag_2O (Kubler[6]). **III** $(COCl)_2$ (Adams and Ulich[7]). Compounds **9** and **13**. For details see Rozancev[8,9]. **IV** $(EtO)_2POCH_2COOC_2H_5$; NaH, DME. **V** H_2; PtO_2; EtOH; HCl. **VI** $LiAlH_4$; Et_2O. **VII** H_2O_2; Na_2WO_4; EDTA.

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