

[A0053]

Synthesis and Structure of Bicyclic Imides and Dithioimides Related to Santenone

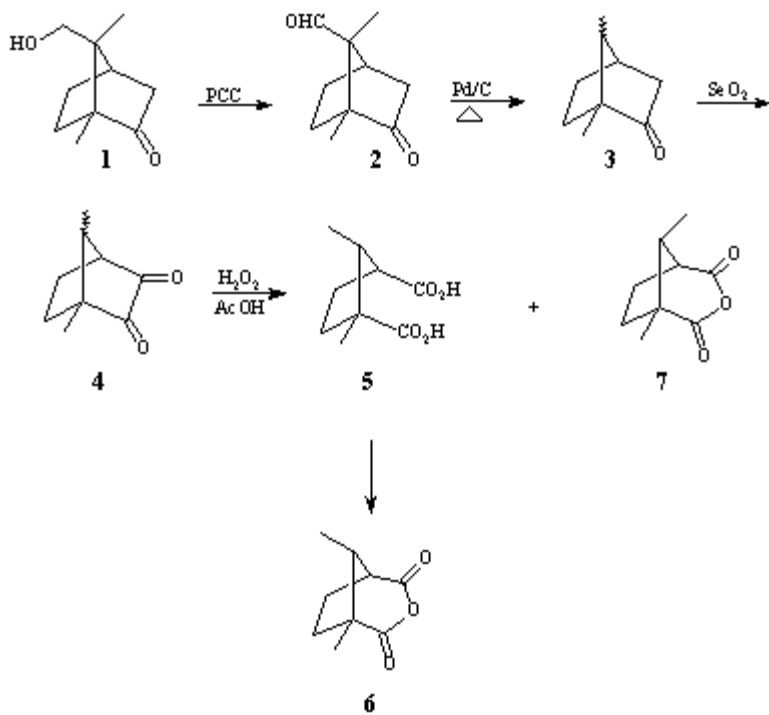
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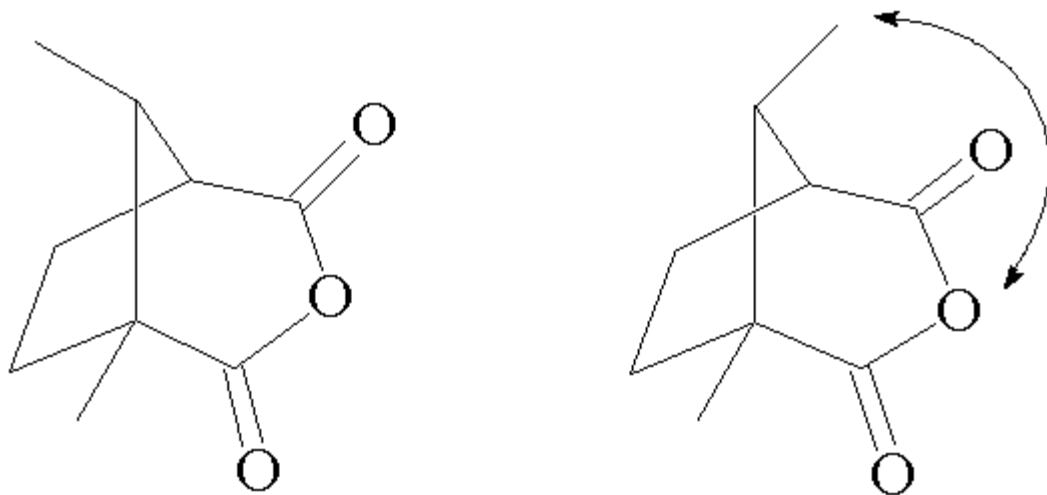
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A close structural relationship between - and -santenones, occurring in Indian sandalwood (*Santalum album*), results in serious difficulties in the preparation of their derivatives in a pure form.^{1,2}



Starting from -hydroxycamphor **1**, a mixture of - and -santenones **3** was prepared by decarbonylation of the corresponding aldehyde **2**. Due to a strong steric effect of C-7 substituent, oxidation of diketone **4** facilitates differentiation of two stereoisomers; resulting -anhydride immediately hydrolyses to acid **5** whereas -anhydride **6** is much less reactive.



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The X-ray structure of **7** showed pronounced non-planarity of the anhydride chromophore (the C-O-C=O torsional angles are of -174.8 and 173.9). This is apparently due to an interaction of the methyl group at C-8 with the chromophore. On the contrary, the anhydride group in **6** is essentially planar (the C-O-C=O is of 179.3 and 177.9).

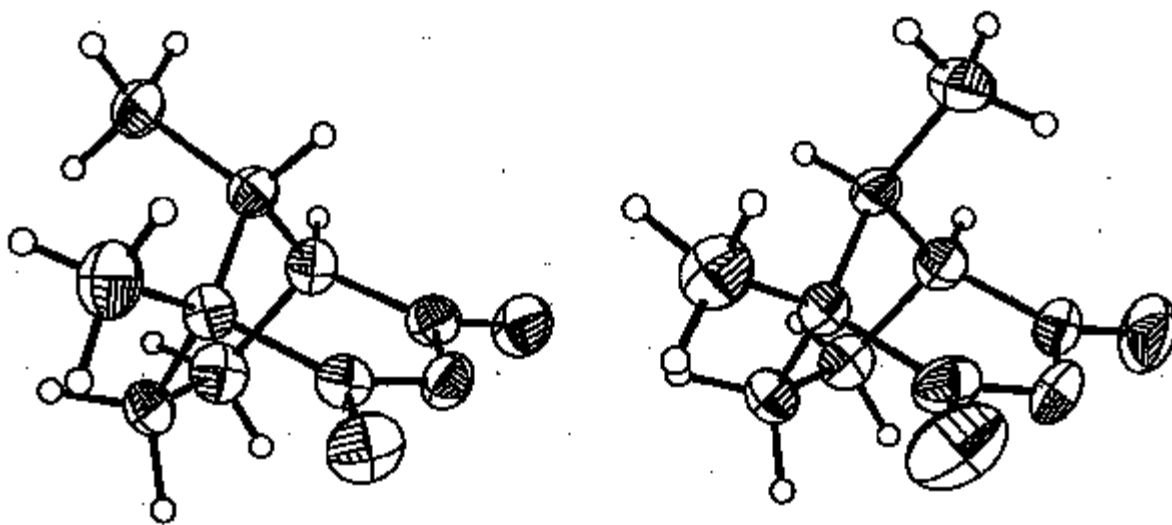
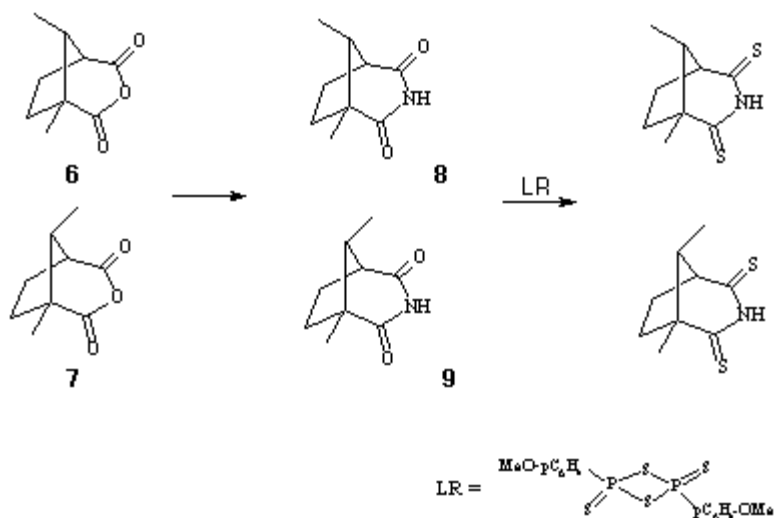
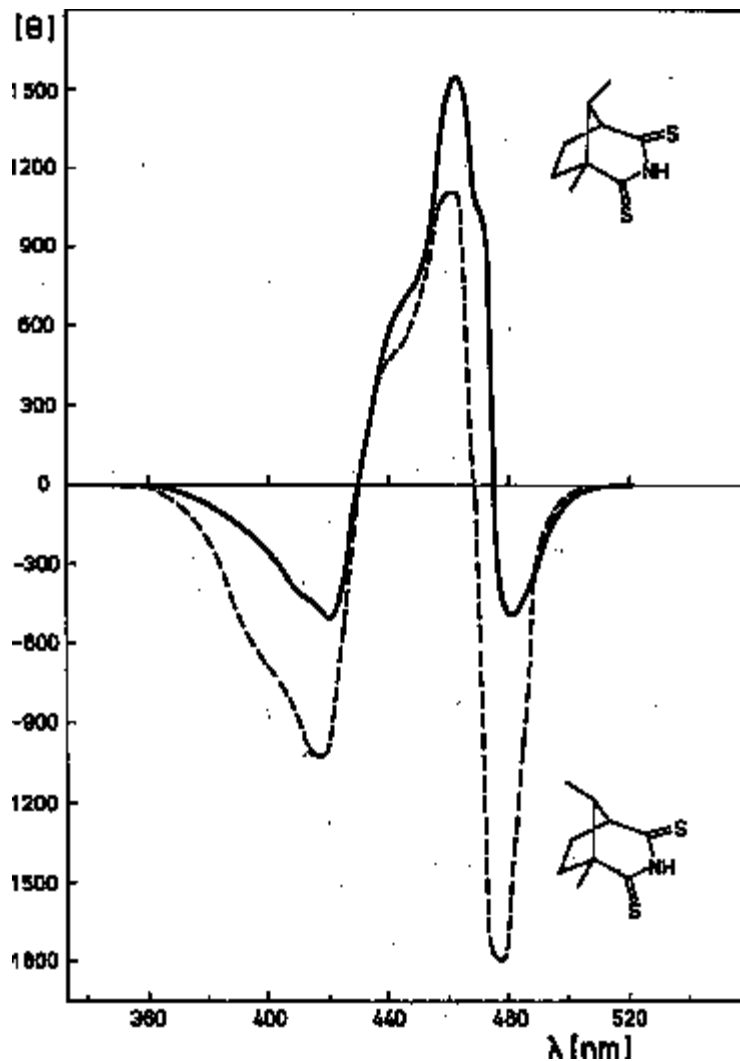


Fig. 1 X-ray crystallographic structure of **6**. Fig.2 X-ray crystallographic structure of **7**.



Similar behaviour is expected for the related dithioimides **10** and **11**, obtained by reaction of corresponding imides with Lawesson's reagent. Therefore the long-wavelength negative $n \rightarrow \pi^*$ Cotton effect can be attributed to the planar chromophore whereas the positive one to the planar arrangement of the dithioimide moiety (cf., dithiocamphorimide spectrum).



The CD spectra of dithioimides **10**, **11**, obtained by reaction of corresponding imides with Lawesson's reagent, are strongly influenced by orientation of the methyl group at C-8.

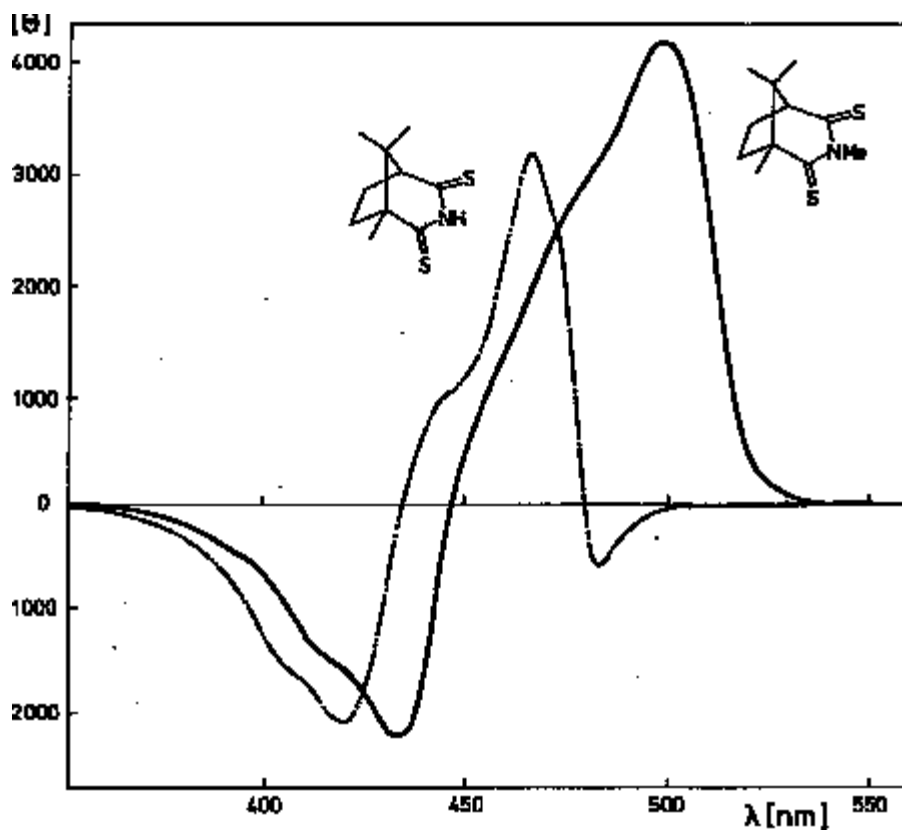
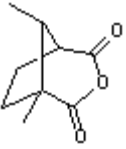
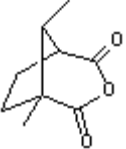
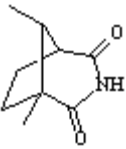
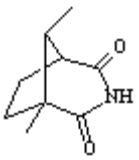
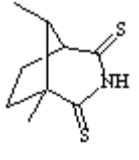
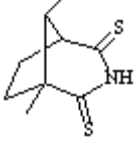


Table 1. Analytical data of compounds **6** - **11**.

	mp. [C]	$[\alpha]_D^{21}$	$^1\text{H NMR (CHCl}_3\text{):}$ [ppm]	$^{13}\text{C NMR (CHCl}_3\text{):}$ [ppm]
 6	127	-17.5 (c 4.0, C_6H_6)	2.95 (d, 1H), 2.32 (m, 2H), 2.1-1.9 (m, 3H), 1.35 (s, 3H), 0.98 (d, 3H)	172.8, 170.1, 50.9, 49.2, 40.8, 31.8, 25.2, 16.4, 12.4
 7	109- 111	+ 6.4 (c 1.8, C_6H_6)	3.10 (dd, 1H), 2.25-2.10 (m, 2H), 2.0-1.85 (m, 3H), 1.34 (s, 3H), 1.06(d, 3H)	171.8, 170.0, 50.3, 49.2, 43.8, 34.9, 25.4, 18.3, 11.3
 8	156- 158	- 8.7 (c 3.3, CHCl_3)	7.78 (br s, 1H), 2.75 (dd, 1H), 2.30 (m, 1H), 2.26 (q, 1H), 1.90 (m, 4H), 1.27 (s, 3H), 0.96 (d, 3H)	178.9, 176.9, 51.4, 42.8, 32.5, 25.9, 15.5, 13.2
	147- 148	+12.5 (c 2.0,	8.05 (br s, 1H), 2.92 (m, 1H), 2.2-1.8 (m, 5H), 1.26 (s, 3H), 1.01 (d, 3H)	177.5, 176.4, 50.6, 50.4, 45.5, 35.7, 26.2, 17.5, 10.7

 9		CHCl ₃)		
 10	69	-45.4 (c 1.4, C ₆ H ₆)	10.5 (br s, 1H), 3.41 (d, 1H), 2.39 (m, 1H), 2.26 (q, 1H), 1.97 (m, 3H), 1.01 (d, 3H),	215.5, 210.8, 61.0, 57.7, 43.8, 36.4, 29.8, 20.6, 14.4
 11	82	+31.0 (c 1.0, C ₆ H ₆)	10.48 (br s, 1H), 3.56 (dd, 1H), 2.3-1.9 (m, 5H), 1.44 (s, 3H), 0.98 (d, 3H)	213.3, 209.3, 59.9, 56.2, 46.6, 39.7, 30.2, 23.1, 10.2

This work was supported by Committee of Scientific Research

1. J. L. Simonsen "*The Terpenes*", Cambridge University Press, 1949, vol. II, p. 257.
2. *Rodd's Chemistry of Carbon Compounds*, S. Coffey, Ed., Elsevier, Amsterdam, 1969, vol. IIC, p. 187.

Comments

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