

STEREOCHEMISTRY OF (+)- α -YLANGENE

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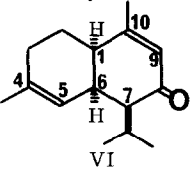
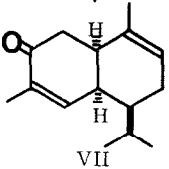
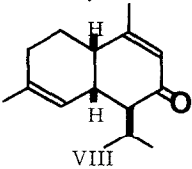
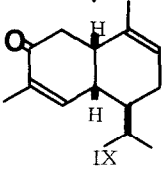
The structure of a sesquiterpene hydrocarbon, α -ylangene, was decided in 1965 by Šorm and his co-workers as shown by the formula (I)⁽¹⁾, which was a stereoisomer of α -copaene (II) as regards the orientation of the isopropyl group at C-7, but its absolute configuration has been left to be determined. Previously, we reported the acid catalyzed isomerization of (+)- α -ylangene and (-)- α -copaene and related them with (-)- α - and (-)- δ -amorphene, (-)- α -muurolene and (+)- δ -cadinene⁽²⁾, the absolute configuration of the latter two have already been established.

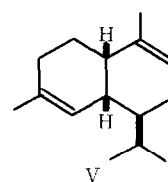
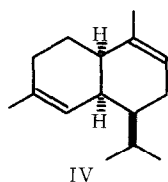
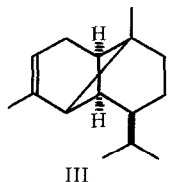
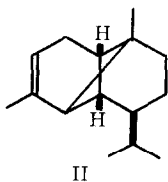
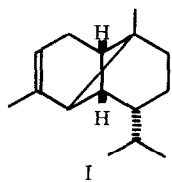
In this communication, we wish to add the elucidation of the absolute configuration of (+)- α -ylangene (III) based upon the extension of the previous communication.

(-)- α -Amorphene (IV), $[\alpha]_D^{25} -127.6^\circ$, obtained from (+)- α -ylangene by acid catalyzed isomerization was oxidized in carbon tetrachloride with tert-butyl chromate in the presence of acetic acid and acetic anhydride at 50°. Two conjugated monoketones, (VI) and (VII), were obtained after purification by column chromatography over silica gel and GLC separation. The physical and spectral data of these ketones are shown in the Table. The constitution of the ketone (VI) was deduced from the fact that 1), its i. r. spectrum lacks the absorption band at 1420cm^{-1} due to an active methylene group adjacent to a carbonyl group, 2), in its mass spectrum, the ion M-42 (m/e 186) formed via the McLafferty rearrangement is more abundant than the ion M-43 (m/e 185), 3), the n.m.r. signals are reasonable for this structure.

TABLE

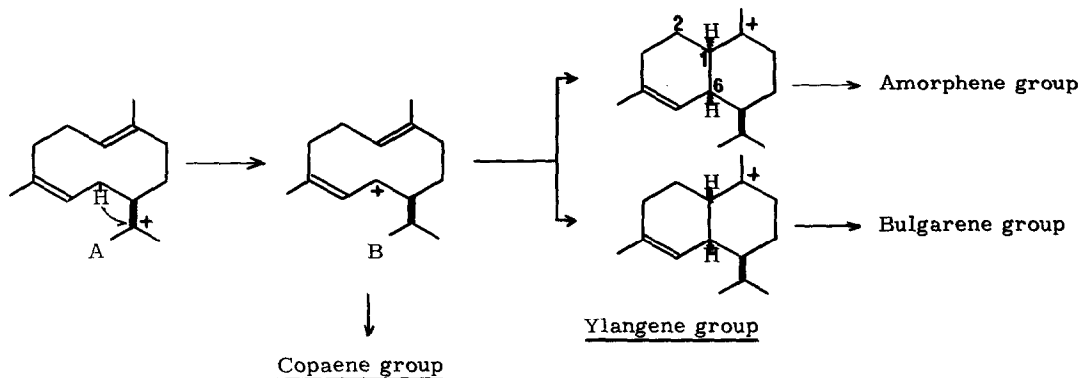
Physical and spectral data of ketones VI, VII, VIII and IX.

	(-)- α -amorphene		(-)- α -muurolene	
				
$[\alpha]_D$	-24.7°	+20.0°	+42.1°	-42.9°
UV: λ_{max} n-hexane				
$m\mu$ (ϵ)	226 (9,800)	231 (9,000)	237 (11,300)	240 (9,200)
IR: cm^{-1}	1670, 1630 (sh.)	1670, 1635 (sh.) 1420	1660, 1630 (sh.)	1670, 1630 (sh.) 1420
MS: r.i. (%)	all compounds exhibit M^+ ion at m/e 218 ($C_{15}H_{22}O$)			
M-42	65.5	12.5	60.0	19.5
M-43	47.5	33.0	38.0	74.5
NMR: δ CCl_4 ppm				
isopropyl	0.90 (d. 6.0)	0.98 (d. 6.0)	0.86 (d. 6.0)	0.92 (d. 6.0)
	1.00 (d. 6.0)	1.00 (d. 6.0)	1.05 (d. 6.0)	0.95 (d. 6.0)
C-4 methyl	1.57	1.67	1.62	1.77
C-5 H	4.98	6.40	5.17	6.73
C-9 H	5.65	5.35	5.60	5.43
C-10 methyl	1.87	1.60	1.91	1.71



(-)- α -Muurolene (V), $[\alpha]_D -50.4^\circ$, isolated from the oil of Chamaecyparis obtusa, was oxidized under the same condition to yield two conjugated monoketones, (VIII) and (IX), and their structures were decided by the same reasons as above. Treatment of the ketone (VI) with basic alumina impregnated with potassium hydroxide⁽³⁾ afforded a mixture of isomerized products, from which, after purification by thin layer chromatography, a ketone was isolated which showed the identical i. r. spectrum, R_t in GLC and R_f in TLC with those of the ketone (VIII) from (-)- α -muurolene. This fact indicates that isomerization of the ketone (VI) at the isopropyl group took place. This epimerization product exhibits optical rotation value, $[\alpha]_D -39.7^\circ$, opposite to that of the ketone (VIII), $[\alpha]_D +42.1^\circ$, and the optical rotatory dispersion curves of these ketones showed also opposite Cotton effects. Accordingly, this epimerization product is the antipode of VIII. Thus, the absolute configurations of (-)- α -amorphene and (+)- α -ylangene are shown by the formula (IV) and (III), respectively.

It is remarkable that most compounds of not only cadalene but selinene, elemene or guaiene type found in nature carry the β -oriented isopropyl group. This suggests that a single or closely related precursor must be involved in the biogenesis of these compounds. (+)- α -Ylangene, as well as other hydrocarbons of ylangene group, is associated with the hydrocarbons of (-)- α -copaene group in several essential oils and now we partially revise the previously mentioned biosynthetic route of sesquiterpenoids of ylangene group⁽²⁾. The intermediate A changes into an intermediate B by 1,3-hydride shift and two type of compounds having α - and β -hydrogen atom at C-6, respectively, may be derived from the intermediate B.



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