Tetrahedron Letters No.27, pp. 3209-3214, 1966. Pergamon Press Ltd.
Printed in Great Britain.

THE ABSOLUTE STEREOSTRUCTURE OF α- AND β-BOURBONENE, SESQUITERPENIC HYDROCARBONS FROM THE ESSENTIAL OIL GERANIUM BOURBON

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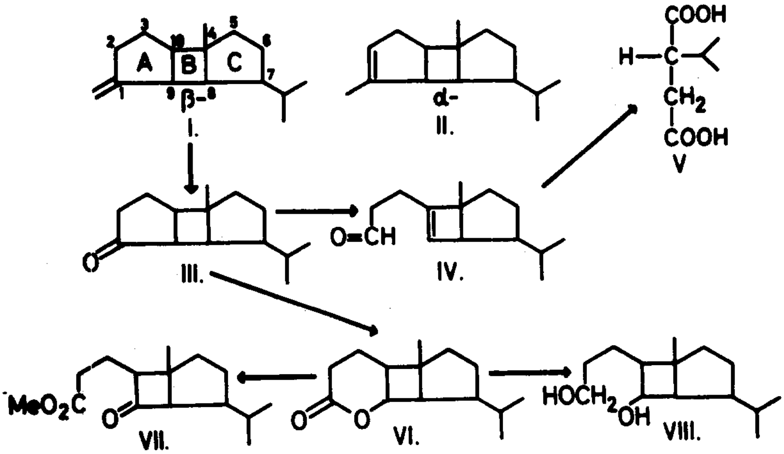
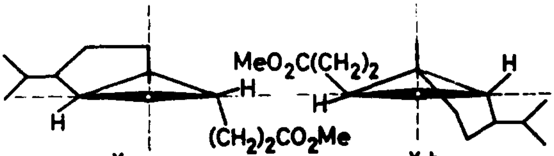
(Received 12 May 1966)

In the recent communication[1] we reported the isolation of both bourbonenes and proved the structure I and II for them. In this article we are going to produce evidence of the absolute configuration of both compounds studied (for their correlation see Ref. 1). From the ketone III prepared the unsaturated aldehyde IV (see scheme I) gave on oxidation with nitric acid a mixture of dibasic acids, the main constituent of it being the (+)-D-isopropyl-succinic acid[2], $[\alpha]_D^{20}$ + 16°, m.p. 85-7° (V), which was isolated by means of preparative paper chromatography. Thus the absolute configuration of assymetric carbon C7 was established. As the p.m.r. spectra of the compounds IV, VI and VIII showed, the coupling constant between H7 and H8 is relatively small. In all compounds H8 forms a broad unresolved signal with half line width $w_H \approx 10$ c.p.s. (after decoupling from H9 $w_H \approx 5$ c.p.s., thus showing that long-range couplings are present). Hence, as can be seen from an inspection of a Dreiding model, the protons H8 and H7

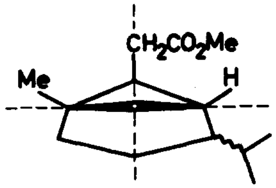


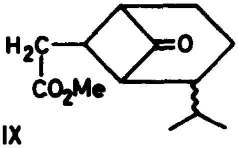
Scheme I.

cannot be eclipsed and therefore must be trans. In this way the cis configuration of isopropyl and the C4 methyl groups was established. This conclusion was further confirmed by means of o.r.d. analysis of the keto methylester VII, which was prepared by hydrolysis of lactone VI, esterification of the formed hydroxy acid with diazomethane to the ester and oxidation of the last named with Brown's reagent (compounds VII exhibited i.r. absorption bands in the carbonyl area at 1738 and 1778 cm^{-1}). The o.r.d. curve of VII showed strongly positive Cotton effect ($[\phi]_{400}$ $+ 530^{\circ}$, $[\phi]_{326}$ $+ 4700^{\circ}$, $[\phi]_{306}$ 0°, $[\phi]_{282}$ $- 5420^{\circ}$, $[\phi]_{240}$ $- 3515^{\circ}$). It has been shown recently[3] that the octant rule is of value even for dissymetric cyclobutanones, and circular dichroism curves were in good agreement with predicted values on the basis of this rule. In the same way, the o.r.d. curve of keto esters IX derived from copaene and ylangene showed positive Cotton effect (copaene: $[\phi]_{589}$ + 0.01°, $[\phi]_{310}$ + 1.7°, $[\phi]_{298}$ 0°, $[\phi]_{272}$ - 2.0°; ylangene: $[\phi]_{589}$ + 0.2°, $[\phi]_{308}$ + 4.9°, $[\phi]_{290}$ 0°, $[\phi]_{272}$ - 3.5°) in good agreement with prediction, thus confirming the utility of the octant rule in more complicated cases[4]. The Cotton effect of VII agrees well with the above assignment of absolute configuration; that both possible conformations of distorted cyclobutane have the same effect upon the sign of Cotton effect can be seen from octant diagrams Xa,b.



Xa Xb

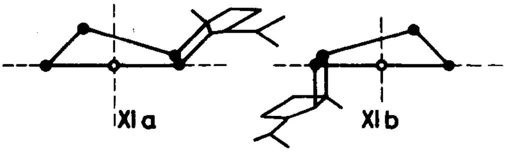




IX

Moreover, it could be deduced from these diagrams, that the 2-methoxy carbonylethyl group should be attached to the cyclobutane ring in trans position with respect to the cycle C and hence the ring A should be trans to the cycle C in I or II, both these compounds thus being in "chair-like" form.

This conclusion is confirmed by the o.r.d. curve of ketone III showing strongly negative Cotton effect ($[\phi]_{400}$ - 1140°, $[\phi]_{329}$ - 7540°, $[\phi]_{298}$ 0°, $[\phi]_{277}$ + 7220°, $[\phi]_{230}$ + 2746°) that can be satisfactorily explained only on the assumption of "chair" configuration of both five-membered rings (the ring A being in an envelope conformation) attached to the cyclobutane. The respective octant diagrams can be drawn as XIa,b.


XIa XIb

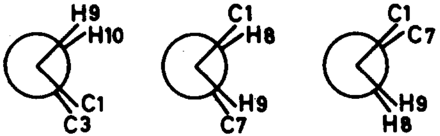
Compatible with these conclusion are the vicinal coupling constants of H9 proton in p.m.r. spectra of the compounds VI and VIII (see table 1). The values of vicinal interactions on cyclobutane can be explained only with difficulty as they are quite sensitive to the geometry of the four-membered ring. It was shown in the case of fluorocyclobutanes[5] that the effects of a "static" and "dynamic" coplanarity affect especially both trans interactions (H-F). In the p.m.r. spectrum of anemonine[6]

Table 1

H9 and H8 τ-values and coupling constants (HA 100, $CDCl_3$)

	H9	H8	$J_{9,10}$	$J_{9,8}$
IV	4.41	7.57	-	0.8
VI	5.55	7.85	7.5	4.0
VIII	6.05	8.28	6.5	2.0

whose cyclobutane occurs in twisted conformation (angle twist = 10°), the two trans H-H interactions, 10.72 and 2.24 c.p.s., were found. Conia et al.[7] analyzed p.m.r. spectra of a number of various substituted cyclobutanones and found all vicinal interactions ranging from 6.4 to 9.7 c.p.s. Two arrangements of both five-membered rings A and C in α- and β-bourbonene with respect to the four-membered ring may occur in general, a cis ("boat") and a trans ("chair") one. The respective situation at the fragments C9-C8 and C9-C10 is illustrated in Newman projections in scheme II.

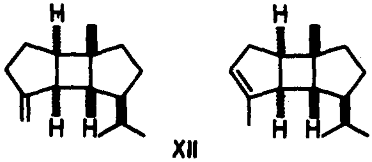


a(*cis*) C9-C10 b(*trans*) C9-C8 c(*cis*) C9-C8

Scheme II.

The configuration of H8 and H9 in the "chair" form (a-b) is trans while that in the "boat" form (a-c) is cis. However, assuming that H9-H10 and H8-H9 are cis (i.e. nearly eclipsed), both J's should be approximately of the same magnitude (6-10 c.p.s.). From the fact that they are not, it can be inferred that the observed J values are better compatible with the chair form, presupposing the existence of the twisted conformation of the cyclobutane ring.[6] Therefore, the absolute configuration of bourbonenes has to be expressed as XII.

All compounds quoted here gave satisfactory elemental analyses. It is hoped that the full experimental details of



XII

the present as well as the preceding communication[1] will be published in Tetrahedron in the near future.

Acknowgledgement. The authors wish to thank Dr I.Frič for the measurement of optical rotation and of o.r.d. curves on an automatic Jasco spectropolarimeter (ORD/UV-5). One of us (Z.S.) expresses his gratitude to Varian A.G., Zurich, Switzerland, for enabling him to run the p.m.r. spectra on an HA-100 instrument.

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