

THE STRUCTURE OF  $\alpha$ - AND  $\beta$ -BOURBONENE, SESQUITERPENIC  
HYDROCARBONS FROM THE ESSENTIAL OIL GERANIUM BOURBON.

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(Received 4 December 1965)

In the course of recent studies on the composition of the essential oil Geranium Bourbon in the Research Laboratory of Givaudan, two unknown tricyclic hydrocarbons (1)  $C_{15}H_{24}$  have been isolated. The first one (I;  $d_4^{20}$  0,8948,  $n_D^{22}$  1.4896,  $[\alpha]_D^{20}$  -92.12°) showed infrared absorption bands at 888, 1662 and 3080  $cm^{-1}$  ( $=CH_2$ ) and a doublet at 1376 and 1388  $cm^{-1}$  ( $-CH/CH_3/2$ ). The p.m.r. spectrum (A-60) confirmed the presence of an exomethylene group (5.3 $\tau$ , 2H, a broadened signal with fine structure due to allylic splitting by  $\alpha$ -protons),  $\Rightarrow C-CH_3$  (8.9 $\tau$ , 3H, sharp singlet) and  $-CH/CH_3/2$  group (6H, an asymmetric doublet

\* Some p.m.r. spectra were recorded on a Varian HA-100 spectrometer during the summer visit of Z.S. in the Research Laboratory of Varian A.G., Zürich, Switzerland.

centered at  $9.11\tau$  with  $J=5$  c.p.s., typical for free-rotating isopropyl group of an  $A_6B$  type); the spectrum exhibited three separate regions of protons of the saturated portion of the molecule, showing the relative integrated areas  $4H$  ( $7.3-7.9\tau$ ):  $9H$  ( $7.9-8.8\tau$ ):  $9H$  ( $8.8-9.3\tau$ ). On catalytic hydrogenation using platinum catalyst in acetic acid, I afforded a saturated dihydro derivative  $C_{15}H_{26}$  (II;  $d_4^{20}$  0.8929,  $n_D^{20}$  1.4759,  $[\alpha]_D^{20}$   $-6.44^\circ$ ), thereby establishing the tricyclic nature of I. The infrared spectrum of II showed a doublet at  $1371$  and  $1383$   $cm^{-1}$ ; it was different from any of the spectra of known tricyclic sesquiterpenic hydrocarbons (2).

The second tricyclic hydrocarbon (III;  $d_4^{20}$  0.9022,  $n_D^{20}$  1.4869,  $[\alpha]_D^{20}$   $+24.7^\circ$ ) occurred in the essential oil in trace amounts. Its infrared absorption bands at  $805$  and  $1650$   $cm^{-1}$  indicated the presence of a trisubstituted double bond; it exhibited also a doublet at  $1368$  and  $1382$   $cm^{-1}$ . According to the p.m.r. spectrum a methyl group was attached to this double bond ( $3H$ ,  $8.45\tau$ ); other features of the spectrum were similar to those of I. On hydrogenation in the presence of platinum catalyst in acetic acid, the hydrocarbon III afforded saturated dihydro compound  $C_{15}H_{26}$  identical with saturated hydrocarbon II. As the same type of isomerism is found e.g. in the case of  $\alpha$ - and  $\beta$ -pinene, we named both hydrocarbons  $\alpha$ - and  $\beta$ -bourbonene. Both hydrocarbons were also isolated in our laboratory from the peppermint oil of Bulgarian origin<sup>3</sup>.  $\beta$ -Bourbonene was

transformed to the  $\alpha$ -isomer, too (3).

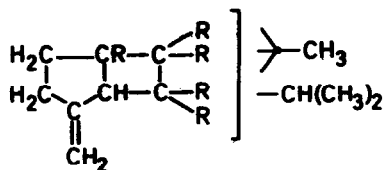
When studying the structures of the mentioned compounds, chemical degradation was combined with physical methods, namely high resolution proton magnetic resonance, used for the characterisation of the products formed. Since the p.m.r. spectra of all the compounds used in our structure proof exhibited typical signals for  $\geq\text{C-CH}_3$  and  $-\text{CH/CH}_3/2$  groups, we shall discuss in more detail only the remaining characteristic signals of a particular compound.

Ozonisation of  $\beta$ -bourbonene in methylene chloride in the presence of pyridine (4) gave a ketone  $\text{C}_{14}\text{H}_{22}\text{O}$  (IV), whose infrared spectrum exhibited strong bands at 1735 and  $1422\text{ cm}^{-1}$  confirming the presence of a  $-\text{CH}_2\text{CO}-$  grouping in a five-membered ring. On treatment with perbenzoic acid in chloroform, the ketone IV gave a lactone  $\text{C}_{14}\text{H}_{22}\text{O}_2$  (V) whose carbonyl group exhibited in the infrared region absorption at  $1745\text{ cm}^{-1}$ , thus proving the presence of a five-membered ring in I. In the p.m.r. spectrum (A-60) of the latter compound a quartet of the proton in the grouping  $-\text{COO-CH-}$  (1H,  $5.55\tau$ ,  $J_1 = 7.5\text{ c.p.s.}$  and  $J_2 = 4\text{ c.p.s.}$ ) was of importance, as it proved that a tertiary carbon atom is present in the other  $\alpha$ -position to the exomethylene group in I. Lithium aluminum hydride reduction of the lactone V yielded a diol  $\text{C}_{14}\text{H}_{26}\text{O}_2$  (VI), the p.m.r. spectrum (HA-100) of which contained signals corresponding to two hydroxyl groups (2H,  $7.46\tau$ , a broadened singlet,

confirmed by exchange with  $D_2O$ ), signals of a proton in  $HO-\underline{CH}$ - (1H, a quartet at  $6.05\tau$ ,  $J_1 = 6.5$  c.p.s. and  $J_2 = 2.0$  c.p.s.) and signals of protons in  $HO-\underline{CH}_2$ - (2H, an unresolved multiplet centered at  $6.39\tau$ ). The signals of these protons did not show any sharpening of the lines on exchange reaction with  $D_2O$ . The splitting of the signal of the  $HO-\underline{CH}_2$ - group gave clear evidence that a  $HO-\underline{CH}_2-\underline{CH}_2-$  grouping was present in this molecule, and hence the grouping  $-\underline{CH}_2-\underline{CH}_2-\overset{\text{H}}{\underset{\text{CH}_2}{\text{C}}}-\underline{CH}-$  must be present also in the original molecule I.

Furthermore, frequency-swept-decoupling experiments established that both interactions,  $J_1$  and  $J_2$ , of the proton in  $HO-\underline{CH}$ - took place with protons attached to different carbon atoms. Tosylation of VI gave the ditosylate  $C_{28}H_{38}S_2O_6$ , which on reduction with  $LiAlH_4$  afforded a secondary alcohol  $C_{14}H_{26}O$ . Oxidation of the latter product with Brown's reagent (5) gave a ketone  $C_{14}H_{24}O$ , the infrared spectrum of which exhibited an absorption band at  $1776\text{ cm}^{-1}$  due to a carbonyl group in a four-membered ring. The presence of the four-membered ring was likely also from the p.m.r. spectra of  $\beta$ -bourbonene (I) and its dihydro derivative II. (In addition to the signals of the three allylic protons in the p.m.r. spectrum of I - see the discussion of the p.m.r. spectrum of VI-, the p.m.r. spectra of both compounds in question contained some other protons in the allylic area). In view of these results, the partial structure I, where R represent unknown

substituents, can be assigned to  $\beta$ -bourbonene.

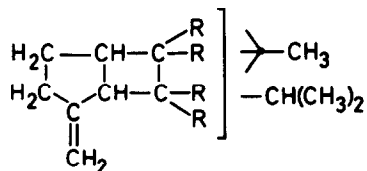


1

In order to prove the arrangement of the atoms in the whole five-membered ring, we reduced the ketone IV with lithium aluminum hydride and obtained an alcohol  $\text{C}_{14}\text{H}_{24}\text{O}$ , m.p.  $82^\circ$ , which was dehydrated on heating with phthalic anhydride to an olefin  $\text{C}_{14}\text{H}_{22}$  (VII). The p.m.r. spectrum of the latter (HA-100) contained signals of vinyl protons (2H,  $4.23\tau$ ) and signals of three allylic protons in the  $7.2\text{--}7.65\tau$  region. Frequency-swept-decoupling experiments confirmed unambiguously the presence of these protons and the simultaneous irradiation of the allylic protons at  $7.35\tau$  (1H) and  $7.65\tau$  (2H) established also the presence of a five-membered ring olefin ( $J_{\text{cis}} = 5.5$  c.p.s.). On treatment with osmium tetroxide, VII yielded a diol  $\text{C}_{14}\text{H}_{24}\text{O}_2$  (VIII, m.p.  $83\text{--}4^\circ$ ) whose p.m.r. spectrum (HA-100) exhibited a broad signal of two hydroxyl groups (2H, at  $7.0\tau$ ; confirmed by exchange with  $\text{D}_2\text{O}$ ), signals of two  $\text{---}\text{CH}_2\text{---}\text{OH}$  protons at  $6.21\tau$  (a doublet, 1H,  $J = 4.5$  c.p.s.) and at  $5.58\tau$  (1H, a broad unresolved signal, giving rise on exchange with  $\text{D}_2\text{O}$  to a symmetrical septet

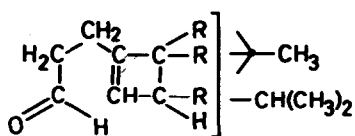
with  $J_1 = 4.5$  c.p.s.,  $J_2 = 7.0$  c.p.s. and  $J_3 = 11.0$  c.p.s.). An inspection of a Dreiding model indicated that the existence of the doublet at  $6.21\tau$  can be explained by the presence of one zero vicinal interaction  $\text{HO}-\underline{\text{CH}}-\underline{\text{CH}}$ ; this is compatible with the ortho-junction of the five and four-membered rings.

The p.m.r. spectra of the olefin VII and the diol VIII, (frequency-swept-decoupling and frequency-swept-tickling experiments) enabled us to write the structure more accurately (formula 2).

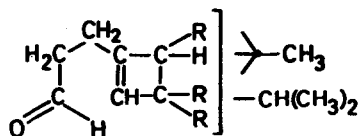


2

The above partial structure was confirmed by u.v. photolysis of the ketone IV in acetic acid. It resulted in the formation of an aldehyde  $\text{C}_{14}\text{H}_{22}\text{O}$  (IX;  $m/e = 206$ , mass spectrometrically) which exhibited an infrared absorption bands at  $1735 \text{ cm}^{-1}$  for carbonyl group and bands at 2710 and  $2810 \text{ cm}^{-1}$  (an aldehydic hydrogen) and contained a double bond ( $1636 \text{ cm}^{-1}$ ) in the four-membered ring (suggested mechanistically) (6). From the above facts two possible partial structures 3 or 4 followed.



3

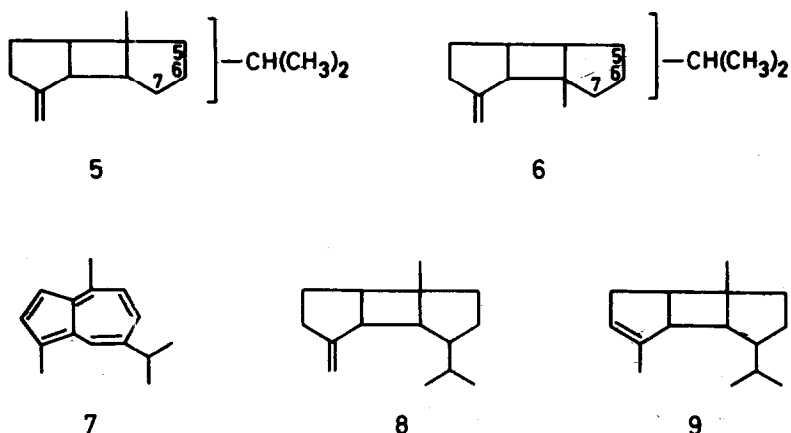


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Frequency-swept-decoupling and frequency-swept-tickling experiments have shown that the p.m.r. spectrum (HA-100) of the latter product (IX) exhibited a signal of an aldehydic proton (1H, 0.22 $\tau$ , a triplet), another of an olefinic proton (1H, 4.41 $\tau$ , a multiplet), signals of three allylic protons at 6.57 $\tau$  (1H) and at 6.78 $\tau$  (2H), and signals of a OHC-CH<sub>2</sub>-C- grouping at 6.4 $\tau$ . As the presence of the grouping OHC-CH<sub>2</sub>-CH<sub>2</sub>- in the molecule IX has been proved by p.m.r. experiments carried out with the diol VIII, an explanation of the existence of three allylic protons in 3 or 4 required the presence of a tetrasubstituted carbon atom in  $\alpha$ -position to the double bond in the four-membered ring of IX. In this way, indirect evidence for the presence of a four-membered ring and also of the nature of its substituents, was gained.

On this evidence, only two reasonable structures, 5 or 6, for  $\beta$ -bourbonene could be written. However, following the regular isoprene rule ("head to tail"

arrangement), the most probable structure was 8 having the isopropyl group at C<sub>7</sub>. The latter structure (8) could be explained formally as a product of intramolecular cyclization of the guaiane skeleton. We attempted therefore to dehydrogenate I with selenium. It gave guaiazulene (7; trinitrobenzene adduct m.p. 153°, undepressed on admixture with an authentic specimen) in 10% yield, thus confirming the structure 8 for β-bourbonene (I). On the basis of these facts, α-bourbonene (III) has to be expressed as 9.



Hence, both hydrocarbons represent an additional example of a transformed guaiane skeleton, where the four-membered ring was possibly formed by transannular cyclization of the original seven-membered ring. This is also confirmed by the fact that the essential oil



Geranium Bourbon contains also hydrocarbons of the guaiane type (1) in large amounts together with both bourbonenes.

All compounds quoted here gave satisfactory elemental analyses. The proof of an absolute stereostructure of  $\beta$ -bourbonene is now under study and we hope to publish the results together with full experimental details of the present communication in Collection Czech. Chem. Commun. next year.

Acknowledgement. The authors thank Dr R.B.Bates, University of Illinois, Urbana Ill. for the measurement of p.m.r. spectra on a Varian A-60 instrument. One of us (Z.S.) expresses his gratitude to Varian A.G., Zürich, Switzerland, for enabling him to run the p.m.r. spectra on a HA-100 instrument.

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