Tetrahedron Letters No. 8, pp. 505-511, 1963. Pergamon Press Ltd.
Printed in Great Britain.

# STRUCTURE OF β-BERGAMOTENE

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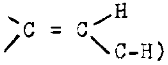
(Received 23 December 1962)

The recent communication by Buchi etal.[1] on the structure of calarene prompts us to record some of the results of our investigation on the constituents of solvent extracted oil of Valeriana Wallichi (Fam. Valerianaceae), a species of Indian origin.

From the hydrocarbon fraction, we have been able to isolate two pure[2] sesquiterpene hydrocarbons by extensive chromatography over alumina. The first of these, Hydrocarbon A, $C_{15}H_{24}$[3] in its NMR spectrum[4] exhibited signals at 4.78(  $\rangle C = C\langle^{H}_{C-H}$)

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[1] G. Buchi, F.Greuter and T.Tokoroyama, Tetrahedron Letters, 18, 827 (1962).

[2] Purity of these compounds was checked through VPC analysis, which showed single peak in each case.

[3] All compounds described gave satisfactory analysis, b.p.refers to bath temperature, $[\alpha]_D$ are for $CHCl_3$; unless otherwise stated.

[4] We are grateful to Drs. A.K.Bose and E.R.Malinowoski of Stevens Institute of Technology,New Jersey, for NMR data and interpretation.

8.93, 8.98, 9.01 (three methyl groups not bonded to any double bond); 9.16 and 9.39 $\tau$ (cyclopropyl protons). Though the infrared spectra of this hydrocarbon and its dihydro derivative showed great similarity with that of calarene and calarane respectively, we were not able to prove its identity with calarene, since the constants reported by Sorm etal.[5] were considerably different from those recorded on our sample. While we were engaged on the structural studies of these compounds, Buchi and coworkers[1] proposed structure (1) for calarene. The physical constants and NMR data recorded by these authors proved the identity of 'Hydrocarbon A' with calarene. Our results regarding its structure will be published shortly.

The major component, Hydrocarbon B, $C_{15}H_{24}$, b.p. 120-130°/1 mm., $[\alpha]_D + 35.8^\circ$ (c, 4.0), $n_D^{27}$ 1.4949, $d_4^{27}$ 0.8841, is a new bicyclic sesquiterpenes containing two double bonds. We propose to name it as β-bergamotene and present evidences to show that it is represented by structure (2) having a novel carbon skeleton. Its infrared spectrum indicates that one of the double bond is methylenic $>C=CH_2$ (3030; 1745, 1653, 874 $cm^{-1}$ typical of β-pinene or camphene) and the other one is trisubstituted (832 $cm^{-1}$) in the form of an isopropylidene group (single peak at 1370 $cm^{-1}$). Infrared spectrum of tetrahydro β-bergamotene b.p. 125-30°/3.5mm. $n_D^{26}$ 1.4683 $(\alpha)_D +27.43^\circ$ (c, 40) obtained by complete hydrogenation of β-bergamotene is not identical with that of any saturated bicyclic sesquiterpenoids[6]

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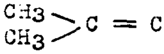
5. F. Sorm, M.Holub, V.Sykora, J.Mlezlva, M.Streibl, J.Pliva, B.Schneider and V.Herout, Coll.Czech.Chem.Comm., 18,512(1953).
6. J.Pliva, M.Horak, V.Herout and F.Sorm, The Terpenes, Coll. of spectra and Physical Constants 1 (1960).

recorded in the literature, though it showed close similarity to that of bergamotane.[7]

Dehydrogenation of β-bergamotene with selenium did not yield any naphthalenic or azulenic hydrocarbon, but gave a product containing a benzenoid system ($\lambda$ max. 265 mμ; $\nu$ max. 1600, 1499, 815 cm$^{-1}$) indicating the presence of six membered ring in β-bergamotene.

The structure of the side chain in β-bergamotene has been established by ozonolysis and other degradative evidences presented below. Selective ozonolysis[8] of β-bergamotene gave acetone (characterised through DNP derivative, m.p. and mixed m.p. 124°) and an unsaturated monoaldehyde (5, R=CHO), $C_{12}H_{18}O$, b.p. 130-140°/0.5 mm., $n_D^{21}$ 1.4945. Infrared spectrum showed bands at: 2710, 1721; 1653, 875 cm$^{-1}$, due to -CHO and $>C=CH_2$ groupings. This suggests that one of the ethylenic linkage is of the type  $(CH_3)_2C=CH-$, a result which has also been supported by NMR data. Oxidation of the aldehyde with silver oxide gave the corresponding acid characterised as its methyl ester (5, R=COOCH$_3$), $C_{13}H_{20}O_2$, b.p. 95-100°/0.5 mm., $n_D^{21}$ 1.4865, $[\alpha]_D$ + 21.58° (c, 3.89). Bands characteristic of terminal methylene group (3060, 1653, 876 cm$^{-1}$) were present in its infrared spectrum. Catalytic hydrogenation of the ester resulted in the uptake of one mol. of hydrogen giving a saturated ester (6), $C_{13}H_{22}O_2$, b.p. 130-35°/4 mm., $n_D^{24}$ 1.4765, $[\alpha]_D$ + 25.32° (c, 7.19); $\nu$ max. 1730, 1190, 1166 cm$^{-1}$.

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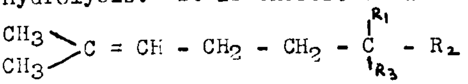
[7] Ref. 6, plate S 193.

[8] We have found that selective ozonolysis of β-santalene also yields bicycloekasantalal.

The methyl ester on treatment with phenyl magnesium bromide followed by dehydration of the resulting diphenyl carbinol with acetic acid-acetic anhydride yielded the hydrocarbon (7), $C_{24}H_{28}$ ($\nu$max. 1600, 1488 $cm^{-1}$; phenyl; $\lambda$max. 251 mμ)[9]. The hydrocarbon (7) on ozonolysis gave a mixture of an aldehyde (8, R=CHO), $\nu$ max. 2710, 1720 $cm^{-1}$, and benzophenone. The former on silver oxide oxidation gave the corresponding acid which was converted to its methyl ester (8, R = $COOCH_3$), b.p. 135-40°/20 mm. with diazomethane. The methyl ester (8, R=$COOCH_3$) was then subjected to another Barbier-Wieland degradation to yield a mixture of an aldehyde (10, R=CHO) $\nu$max. 2710, 1721 $cm^{-1}$ and benzophenone, via the intermediate (9), $C_{23}H_{26}$, ($\nu$max. 1604, 1502 $cm^{-1}$; phenyl; $\lambda$ max. 249.5 mμ).[9]

The presence of an aldehydic group in (10) was confirmed by its conversion to the corresponding tertiary acid (10, R=COOH) and its methyl ester (10, R=$COOCH_3$) which was resistant to hydrolysis. It is therefore safe to conclude the presence of



$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C = CH - CH_2 - CH_2 - \underset{R_3}{\overset{R_1}{C}} - R_2$

grouping in β-bergamotene. ( $R_3$ = $CH_3$, NMR signal at 9.05τ Fig. 1 )

The unsaturated ester (5, R=$COOCH_3$) on reduction with $LiAlH_4$ gave the corresponding alcohol, ozonolysis of which furnished formaldehyde (dimedone derivative, m.p. and mixed m.p. 189° ) and a keto-alcohol (11) having the new carbonyl group in the six membered ring ($\nu$max. 1715 $cm^{-1}$). A band at 1414 $cm^{-1}$ indicated the presence of $-CO-CH_2-$ grouping and hence a $R-\overset{CH_2}{\overset{\|}{C}}-CH_2-$ grouping in the six membered ring of β-bergamotene.

Thus fourteen out of fifteen carbon atoms can be

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[9] The position of $\lambda$max. indicates the presence of the grouping $(Ph)_2 = C = CHR$, cf. J.D.Cocker and T.G.Halsall, J.Chem.Soc. 4262(1956).

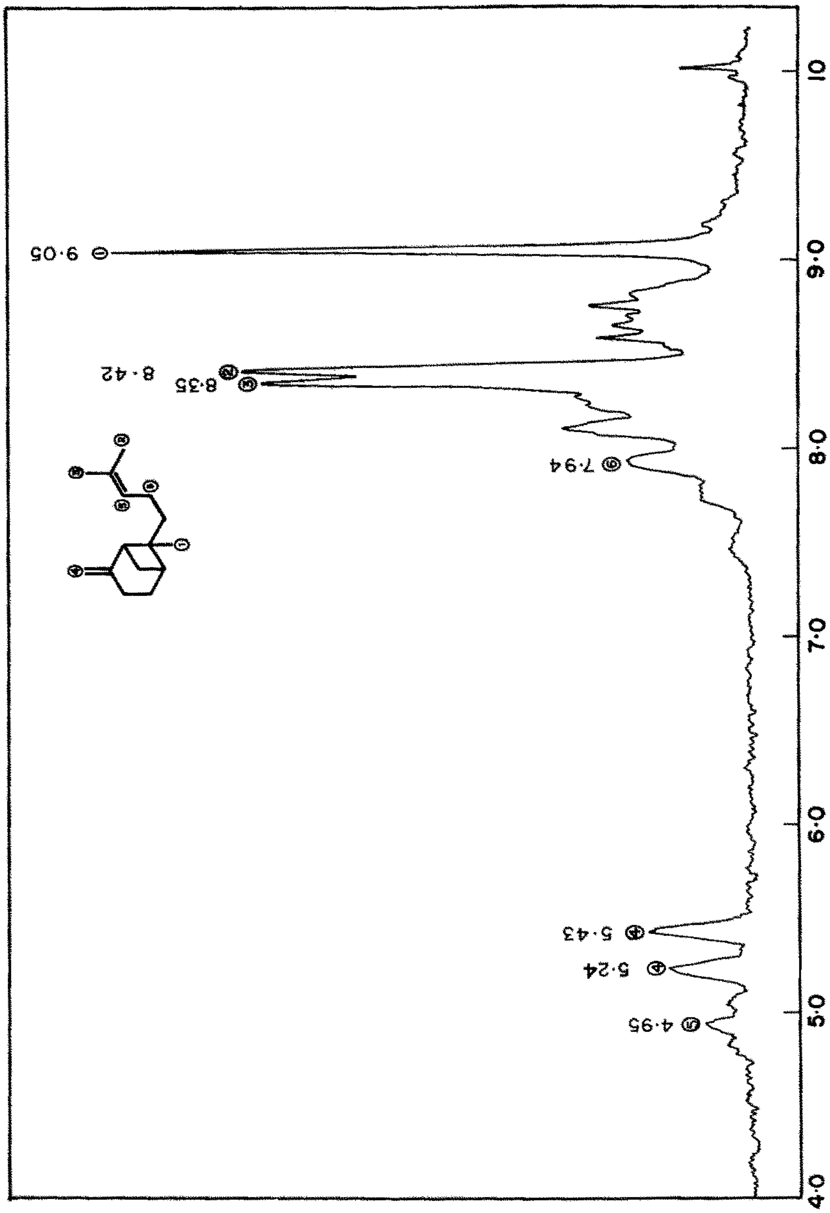
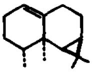


Fig. 1 NMR Spectrum of β-Bergamotene (in $CCl_4$ using TMS as internal standard)

accounted for. Taking into consideration the bicyclic nature and assuming β-bergamotene follows isoprene rule it can be represented by the structures (2) or (3), the former being preferred, because of the stability of tetrahydro β-bergamotene (4), towards anhydrous hydrogen chloride.

A comparative study of the NMR spectra* of β-bergamotene, tetrahydro β-bergamotene, α-santalene, dihydro$\overset{\alpha\text{-}}{\wedge}$santalene, β-santalene, and tetrahydro β-santalene fully supports the structure (2) for β-bergamotene. Positions of the main peaks and assignments for β-bergamotene are given in Fig.1.

It is also felt that in conformity with the accepted nomenclature of the pinenes, the closely related compound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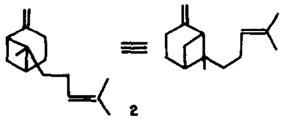
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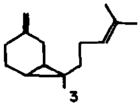
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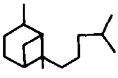
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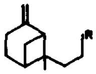
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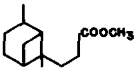
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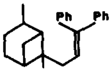
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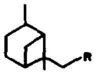
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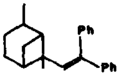
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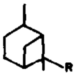
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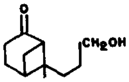
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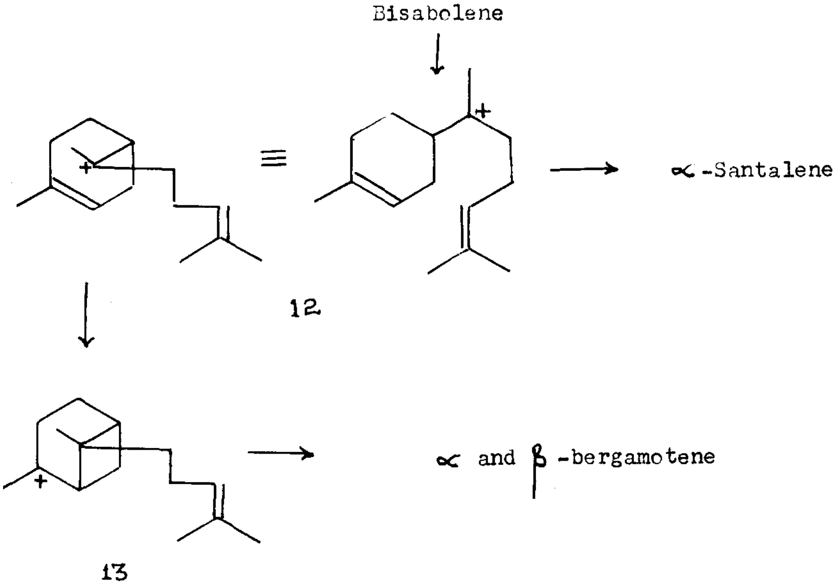
* All NMR measurements were carried out by Dr. R.B.Bates,

bergamotene previously examined by Sorm and collaborators[10] should be named as α-bergamotene, chemical proof for the structure of which does not appear to be available in the existing literature.

β-Bergamotene may have biogenetic relationship to bisabolene, and can be derived from it according to the following scheme (Formulae 12-13).



According to the scheme suggested by Ruzicka[11] the same cation (12) gives rise to α-santalene.

Additional experiments in support of the structure(2) including its degradative conversion to pinane will be published shortly in a full paper.

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[10] V. Herout, V.Ruzicka, M.Vrany, and F. Sorm, Coll.Czech. Chem.Comm. 15, 373 (1950).

[11] L. Ruzicka, Proc.Chem.Soc. 341 (1959).