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THE NATURE OF SESQUITERPENIC HYDROCARBON CALARENE AND STRUCTURE OF β-GURJUNENE

J. Vrkoč, J. Křepinský, V. Herout and F. Šorm

Institute of Organic Chemistry and Biochemistry

Czechoslovak Academy of Science, Prague

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RECENTLY, Büchi, Greuter and Tokoroyama[1] published their results about structure of calarene (characterised mainly by $[\alpha]_D^{EtOH}$ +58°) isolated from the so called Chinese Spikenard oil (from Nardostachys jatamanis /Roxb/DC.) and allotted structure I for it. The hydrocarbon calarene had been isolated also from sweet-flag oil in this Laboratory[2] nearly ten years ago. Büchi and co-workers[1] elucidated also stereochemistry of aristolone (II), a sesquiterpenic ketone, the constitution of which had been ascertained by Furukawa et al.[3] last year.

We studied independently the structure of calarene, characterised in our case by $[\alpha]_D^{20}$ + 23.6°, which had been newly isolated from the sweet-flag oil (Acorus calamus L.) using the already reported procedure[2]; further, we investigated structure of β-gurjunene (III) obtained from gurjunbalsam

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1 G. Büchi, F. Greuter and Takashi Tokoroyama, Tetrahedron Letters No. 18 827 (1962)

2 F. Sorm, M. Holub, V. Sykora, J. Mleziva, M. Streibl, J. Pliva, B. Schneider and V. Herout, Coll. Czech. Chem. Comm. 18, 512 (1953).

3 S. Furukawa and N. Soma, J. Pharm. Soc. Japan 81, 559 (1961); S. Furukawa, K. Oyamada and N. Soma, Ibid. 81, 565 (1961); S. Furukawa, Ibid. 81, 570 (1961).

(Dipterocarpus sp.)[4 +]. As we arrived independently at the same formula for β-gurjunene as Büchi (l.c.) for calarene and as both the compounds in question according to their physical constants (cf. Table I) and infra-red spectra were not identical, we wish to present our studies about β-gurjunene and calarene from sweet-flag oil.

All three samples of hydrocarbons, i.e. both our samples of calarene (I) and β-gurjunene (III) afford on hydrogenation in the presence of platinum catalyst the same tricyclic hydrocarbon IV (for the physical constants cf. Table I). The same saturated hydrocarbon has been obtained by hydrogenolysis of the ketone aristolone (II)* The infra-red spectra of all samples of saturated hydrocarbons were in perfect accordance as well. Büchi (l.c.), by means of infra-red spectrum, proved the identity of the saturated hydrocarbon from calarene (I) and from aristolone (II); this shows undoubtly an identity of the carbon skeletons of all sesquiterpenic compounds mentioned.

From NMR spectra of β-gurjunene and of our specimen of calarene, which for both compounds are practically identical, follow only two possible alternative structures III and V resp.; the spectra exhibit a broadened peak at 4.82τ due to single hydrogen atom on double bond, and three singlet peaks

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4 Gildemeister E., Hoffmann Fr., Die Ätherischen Öle, Band III a, Akademie Verlag Berlin; p. 308 (1960).

* A sample of gurjunbalsam was kindly supplied by I.F.F. N.V.Zaandam (Holland). We are indebted to Dr. M.G.J. Beets for his kind assistance in this matter.

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Table I

Physical Constants of Sesquiterpenic Hydrocarbons

Name	Origin	$[\alpha]_D^{20}$ (in subst.)	d_4^{20}	n_D^{20}
Calarene I	Spikenard oil[1]	+58° [a]	-	1.5029
	Sweet-flag oil[2]	+18.4°	0.9202	1.4978
	this paper	+23.6°	0.9375	1.5040
β-Gurjunene III	Gurjunbalsam	+81.8°	0.9340	1.5051
Aristolene V		-98.7°	0.9424	1.5047
Saturated hydrocarbon IV	from calarene (Büchi[1])	-53.0° [b]	-	-
	from calarene (this paper)	-45.3°	0.9198	1.4916
	from β-gurjunene	-45.0°	0.9182	1.4940
	from aristolone (Büchi[1])	-48.0° [b]	-	-
	from aristolone (this paper)	-44.9	0.9240	1.4968

[a] measured in EtOH solution; [b] measured in $CHCl_3$ solution

at 8.96, 9.01, 9.03τ due to one angular methyl group and two geminal methyl groups on a cyclopropane ring; a peak at 9.09τ is one of the peaks belonging to a doublet due to methyl group on -CH in a ring; the other band is overlapped by singlets due to methyl groups; a peak at 9.42τ corresponds to hydrogen on a cyclopropane ring and further peaks in this region belong to the second cyclopropane hydrogen which is splitted by hydrogens of neighbouring CH_2 group.

Using the procedure of Büchi (l.c.), we prepared from aristolone the unsaturated hydrocarbon V which we called aristolene (physical constants cf. Table I). Although the hydrocarbon, according to physical constants and infra-red spectrum, was identical with neither of the mentioned hydrocarbons (I and III), on hydrogenation it afforded the same saturated tricyclic hydrocarbon IV.

From all these facts, formula III follows for β-gurjunene, which however, is identical with structure I proposed by Büchi for calarene. This however, is at variance with the fact that both hydrocarbons are different compounds.

We succeeded in separating our (from sweet-flag oil) by means of gas-liquid chromatography (stationary phase: 7% polyethylene adipate on ground unglazed tile[5]) into two components present in a ration of 1:4. Infra-red spectrum of our sample of calarene exhibited, unlike that of β-gurjunene, some additional maxima. These bands, however, are present in the spectrum of aristolene; on superpostion of the spectra of aristolone (V) and of β-gurjunene (III) there may be obtained the spectrum of calarene. The fact that calarene is a mixture was corroborated by preparation of two diols by osmium tetroxide oxidation of the former. The main product of m.p. 144° was, according to infra-red spectrum and mixed melting point, identical with diol VI prepared from β-gurjunene (III); the second diol VII (m.p. 107-108°) was identical with the product prepared from aristolene (V).

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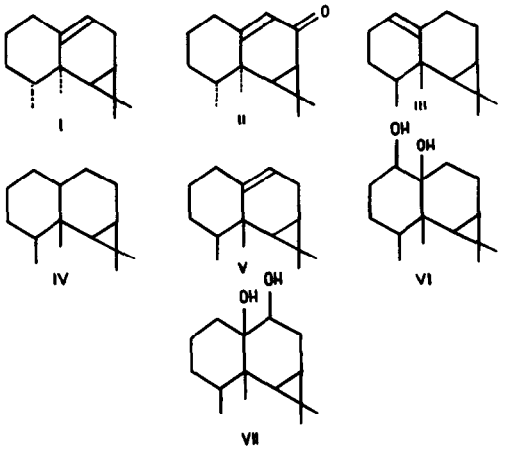
[5] V. Lukes, R. Komers and V. Herout: J. Chromatog. 3, 303 (1960).



Thus we proved that the so called calarene from sweet-flag oil is a mixture of β-gurjunene and aristolene. We suppose that even the hydrocarbon isolated by Büchi (l.c.) from Chinese Spikenard oil, because of its lower optical rotation in comparison with the value of pure β-gurjunene (cf. Table I), might contain a smaller amount of aristolene. As the name β-gurjunene was used far earlier[4], we suppose that the name calarene should be abandoned.

It is hoped to publish this work in full detail in Collection of Czechoslovak Chemical Communications.

The NMR spectrum was measured in the Laboratories of International Flavours and Fragrances Inc., Union Beach, N.J. U.S.A. by the courtesy of Dr. W.T. Somerville. Our thanks are due to Dr. Jonas for the interpretation of NMR spectra and to Dr. J. Pitha for the interpretation of infra-red spectra.