

## CHEMISTRY OF THE NATURAL ORDER CUPRESSALES—XXVI\*

### THE IDENTITY OF JUNIPENE, KUROMATSUENE AND LONGIFOLENE AND OF JUNIPEROL, KUROMATSUOL, MACROCARPOL AND LONGIBORNEOL

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(Received 27 November 1959)

**Abstract**—Kuromatsuene and longifolene are identical with junipene, and kuromatsuol and longiborneol are identical with juniperol.

MATTSON<sup>1</sup> described a sesquiterpene  $C_{15}H_{24}$  called junipene and a sesquiterpene alcohol  $C_{15}H_{26}O$  called juniperol from the bark of *Juniperus communis* L. The well defined crystals of the latter had already been subjected to a crystallographic study by Ramsay.<sup>2</sup>

Later Shinozaki described a sesquiterpene kuromatsuene isolated from the root oil of *Pinus thunbergii* Parlatores (Kuromatsu)<sup>3</sup> and Akiyoshi isolated both kuromatsuene and a sesquiterpene alcohol, kuromatsuol, from the same tree.<sup>4</sup> These papers have remained almost unknown but it can be seen from Tables 1 and 2 that the physical

TABLE 1

No	Name	b.p./mm	$n_D$	$[\alpha]_D$	M.p. of hydrochloride	M.p. of hydrobromide	Source	References
1	Junipene	257/767	1.5030(20°)	41.05°	58.5°	—	Bark of <i>Juniperus communis</i>	1
2	Kuromatsuene	109/7	1.5032(20°)	40.3°	59–60°	—	Root oil of <i>Pinus thunbergii</i>	3
3	Junipene	115/10	1.5032(23°)	37°	58–59°	—	Bark of <i>Juniperus communis</i>	this work
4	Kuromatsuene	127.5– 128.5/18	1.5043(18.5°)	—	—	71–72°	Oleoresin of <i>Pinus densiflora</i>	unpublished
5	Longifolene	254–256/706 150–151/36	1.4950(30°)	42.7°	59–60°	69–70°	Various pines	10

constants of kuromatsuene and kuromatsuol are similar to those of Mattson's junipene and juniperol.

During an investigation of the leaf oil of *Cupressus macrocarpa* Hartweg, Briggs and Sutherland<sup>5</sup> isolated the sesquiterpene alcohol macrocarpol, which later was also obtained from the heartwood of *Dacrydium cupressinum*, Solander (Rimu), by Brandt

\* Part XXV, *Acta Chem. Scand.* in press.

<sup>1</sup> G. Mattson, *Bidr. Finl. Nat. Folk.* H 72, 1 (1913).

<sup>2</sup> H. Ramsay, *Z. Kryst. Min.* 46, 281 (1909).

<sup>3</sup> E. Shinozaki, *J. Ind. Chem. Soc., Japan* 763 (1918).

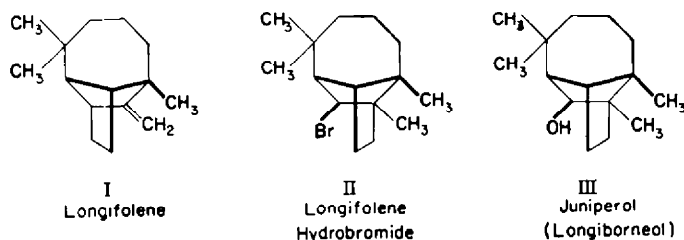
<sup>4</sup> S. Akiyoshi, *Rep. Imp. Ind. Res. Inst., Osaka, Japan* 17, No. 10 (1937).

<sup>5</sup> L. H. Briggs and M. D. Sutherland, *J. Org. Chem.* 7, 397 (1942).

and Thomas.<sup>6</sup> This sesquiterpene alcohol was, subsequently, shown to be identical with juniperol by Erdtman and Thomas.<sup>7</sup>

During the course of an investigation of the sesquiterpene fractions of the oleoresin of *Pinus densiflora* Siebold et Zuccarini (Akamatsu) and of *Pinus Formosana* Hayata, kuromatsuene and kuromatsuol were isolated by one of us (T. K. with T. Tsutsui unpublished. Compare also Ito and Matsumoto).<sup>8</sup> These compounds have now been shown to be identical with junipene and juniperol respectively which were isolated from a sample of the bark oil of *Juniperus communis* L. At the same time a close similarity was noticed between the reported physical constants of longifolene and longiborneol and those of junipene and juniperol.

Longiborneol (III) was prepared by Naffa and Ourisson starting from longifolene (I) which was converted into longibornyl bromide (II), and then to the corresponding Grignard compound. This when treated with oxygen in ether yielded longiborneol.<sup>9</sup>



Longifolene, longifolene hydrochloride and longiborneol have been compared with junipene, junipene hydrochloride and juniperol. Mixed melting points and a comparison of the infra-red spectra show that longifolene is identical with junipene,

TABLE 2

No	Name	m.p. °	$[\alpha]_D^{20}$	Source	References
6	Juniperol	107	18.4 (CHCl <sub>3</sub> ) 17.8 (C <sub>2</sub> H <sub>5</sub> OH)	Bark of <i>Juniperus communis</i>	1
7	Kuromatsuol	107–108	12.2	Root oil of <i>Pinus thunbergii</i>	4
8	Macrocarpol	110	25.4 (C <sub>2</sub> H <sub>5</sub> OH)	Leaf oil of <i>Cupressus macrocarpa</i>	5
9	Macrocarpol	112	17 (C <sub>2</sub> H <sub>5</sub> OH)	Heartwood of <i>Dacrydium cupressinum</i>	6
10	Juniperol	110	16 (CHCl <sub>3</sub> )	Bark of <i>Juniperus communis</i>	this work unpublished unpublished
11	Juniperol	109–110	17 (CHCl <sub>3</sub> )	Oleoresin of <i>Pinus formosana</i>	
12	Juniperol	105–109	—	Oleoresin of <i>Pinus densiflora</i>	
13	Longiborneol	106–107	21	From longifolene	

that longifolene hydrochloride is identical with junipene hydrochloride and that longiborneol is identical with juniperol. Kuromatsuene and kuromatsuol were similarly identified with longifolene and juniperol respectively.

The physical constants of longifolene (junipene, kuromatsuene) and juniperol (kuromatsuol, macrocarpol, longiborneol) from various sources are shown in Tables 1 and 2.

<sup>6</sup> C. W. Brandt and B. R. Thomas, *N.Z. J. Sci. Tech.* B 33, 30 (1951).

<sup>7</sup> H. Erdtman and B. R. Thomas, *Chem. & Ind.* 384, (1955).

<sup>8</sup> Sh. Ito and T. Matsumoto, *Chem. Abstr.* 49, 15236 (1955).

<sup>9</sup> P. Naffa and G. Ourisson, *Bull. Soc. Chim. Fr.* 5, 1410 (1954); A. Hesse, *Ber. Dtsch. Chem. Ges.* 39, 1151 (1906).

<sup>10</sup> J. L. Simonsen, *The Terpenes* Vol. III, p. 92. Cambridge (1952).

Direct comparisons have been carried out on the following samples: 3 and 5, 4 and 5 (this work); 6 and 9;<sup>7</sup> 8 and 9;<sup>6</sup> 10 and 11; 10, 11 and 13 (this work); 11 and 12 (as 3,5-dinitrobenzoates).

No direct comparison with the products obtained from *P. thunbergii* by Akiyoshi could be made, since these samples were lost during the war. The optical rotation of the juniperol preparations varies considerably. Although juniperol crystallizes well it seems difficult to obtain absolutely pure.

Mattson's name junipene has priority over longifolene which was described by Simonsen in 1920, but it is suggested that the well known name longifolene should be retained for this compound. For the alcohol the name juniperol, as suggested earlier,<sup>7</sup> should be retained instead of macrocarpol (and kuromatsuol and longiborneol).

From a chemotaxonomic point of view it is of interest to note that longifolene is represented in the natural orders Pinales, Cupressales and Podocarpaceae. A biosynthetic relation between longifolene and juniperol appears, of course, to be very probable since they frequently occur together in the same tree.

*Acknowledgements*—The authors would like to thank the U.S. Army and Development Liaison Group under contract number DA-91-591-EUC-1113 for the grant which enabled one of us (T. K.) to take part in this work. We also wish to thank Professor and Mrs. Sørensen, Trondheim and Professor Ourisson for samples of the bark oil of *Juniperus communis* and of longifolene, its hydrochloride and longiborneol.