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STRUCTURE OF CAMPHERENONE AND CAMPHERENOL

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From camphor blue oil, the high boiling fraction of the essential oil from the wood of camphor tree, Cinnamomum camphora Siebold (Lauraceae), we have recently isolated two new sesquiterpenoids for which the names campherenone and campherenol are given. On the basis of the observations which follow, we now wish to propose for campherenone and campherenol the stereostructures I and II, respectively.

Campherenone, $C_{15}H_{24}O$, $[\alpha]_D$ -33.0°, ν^{CCl_4} 1745 and 1415 cm^{-1} (five-membered ring ketone flanked by methylene), shows n.m.r. signals*1 for two tertiary methyl groups and an isopentenyl group (Table I), the latter grouping being confirmed by n.m.d.r. experiments. These data, together with the common occurrence of campherenone with camphor (VI) and α-santalene[1)] in the same plant, lead to the assumption that campherenone may be 8 or 9-isopentenylcamphor. This was supported by the n.m.r. evidence that the line positions of the two tertiary methyl signals in campherenone coincide with those[2)] of the C-9 and C-10 proton signals in camphor (VI) (Table I), suggesting the isopentenyl grouping to be substituted at C-8 of the camphor skeleton. The mass spectrum of campherenone verified structure I, since the cracking pattern is well explained in terms of an isopentenylcamphor.[3,4)]*2 The absolute stereochemistry of campherenone was deduced from the positive Cotton effect in the optical rotatory dispersion curve.[5)]

Campherenol, $C_{15}H_{26}O$, $[\alpha]_D$ -62.1°, ν^{CCl_4} 3650 and 3410 cm^{-1} (hydroxyl), on acetylation formed the acetate (III), $[\alpha]_D$ -23.3°, ν^{CCl_4} 1733 and 1238 cm^{-1} (acetoxyl). Campherenol was oxidized with chromic acid to furnish campherenone, establishing the structure and absolute configuration of campherenol except for the configuration at C-2. Reduction of campherenone with lithium aluminum hydride afforded 2-epi-campherenol (IV), $[\alpha]_D$ +15.3°, ν^{CCl_4} 3650 and 3490 cm^{-1} (hydroxyl), which on acetylation gave the acetate (V), $[\alpha]_D$ +39.2°, ν^{CCl_4} 1732 and 1232 cm^{-1} (acetoxyl). The chemical shifts and splitting patterns of the C-2 hydrogen signals of campherenol, its acetate (III), 2-epi-campherenol (IV), and its acetate (V) are in accord with those[6)] of borneol (VII), its acetate (VIII), isoborneol (IX), and its acetate (X), respectively (Table II), a fact which indicates that the C-2 hydroxyl group of campherenol is α-oriented.

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FOOTNOTES AND REFERENCES

[*1] The n.m.r. spectra were run at 60 Mc. Chemical shifts are given in p.p.m. from internal TMS, and coupling constants (J) in c.p.s. Abbreviation: d=doublet.

[*2] This will be discussed in detail in our forthcoming original paper.

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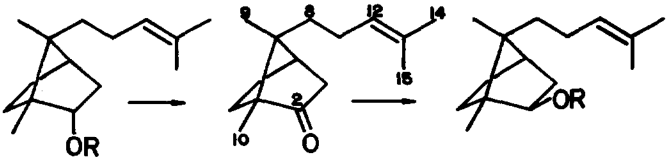
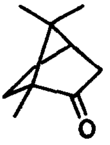


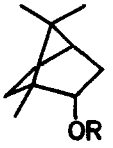
II: R=H
III: R=$COCH_3$

I

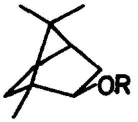
IV: R=H
V: R=$COCH_3$



VI



VII: R=H
VIII: R=$COCH_3$



IX: R=H
X: R=$COCH_3$

Table I. N.m.r. signals of the ketones.

	Campherenone (I)				Camphor (VI)		
Solvent	C-9	C-10	C-14,C-15	C-12	C-8	C-9	C-10
Carbon tetrachloride	0.96	0.85	1.64,1.59	5.03	0.81	0.94	0.84
Chloroform	0.96	0.88	1.64,1.57	5.04	0.83	0.97	0.91
Benzene	0.67	0.90	1.62,1.49	4.98	0.60	0.65	0.89
Pyridine	0.84	0.92	1.64,1.55	5.04	0.70	0.79	0.89

Table II. N.m.r. signals of the C-2 hydrogens of the alcohols and the acetates (CCl_4).

Campherenol (II)	3.97 ddd (J=10,3,1)	Borneol (VII)	3.94 ddd (J=10,4,2)
Campherenyl acetate (III)	4.86 ddd (J=9,3,1)	Bornyl acetate (VIII)	4.81 ddd (J=10,3,2)
2-epi-Campherenol (IV)	3.51 dd (J=5,5)	Isoborneol (IX)	3.51 dd (J=5,5)
2-epi-Campherenyl acetate (V)	4.62 dd (J=7,5)	Isobornyl acetate (X)	4.62 dd (J=5,5)