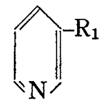
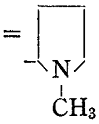
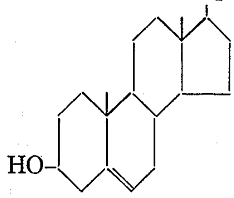
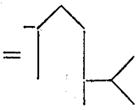
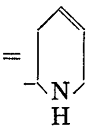
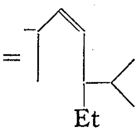
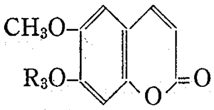
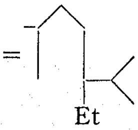
Table I. Constituents in Tobacco Callus

Compound \ Callus		IAA	2,4-D	Compound \ Callus		IAA	2,4-D
 Alkaloids	R_1=  Nicotine	+	−	 Phytosterols	R_2=  Campesterol	−	+
	R_1=  Anatabine	+	−		R_2=  Stigmasterol	−	+
 Phenols	R_3=H Scopoletin	+	+		R_2=  β-Sitosterol	−	+
	R_3=Glucose Scopolin	+	+				

tobacco callus have been shown to be markedly influenced by the supply of IAA and 2,4-D in the nutrient medium.

More detailed chemical and biosynthetic investigations are now in progress to determine the possible causal relationship between the action of IAA and that of 2,4-D in these phenomena.

We are grateful to Dr. E. Tamaki and Dr. E. Masuda of Japan Monopoly Corporation for authentic samples of tobacco alkaloids and tobacco plant, and to Dr. H. Itokawa of Tokyo College of Pharmacy for authentic samples of phytosterols.

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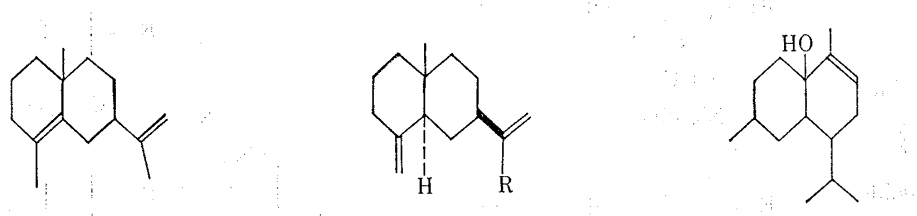
New Constituents of *Chamaecyparis formosensis* Matsum.[1]

During the reinvestigation of the terpenoid constituents of the Benihi tree (*Chamaecyparis formosensis* Matsum., Cupressaceae, grown in Taiwan), a novel nor-sesquiterpenoid, chamaecynone and related compounds were isolatied.[1,2] Chamaecynone and freelinyne reported by Massy-Westropp, *et al.*[3] are the first examples of acetylenic

1) Presented at the general local meeting of the Hokkaido district of the Chemical Society of Japan, at Sapporo, in July, 1965; abstract paper, pp. 11~12.
2) T. Nozoe, Y.S. Cheng, T. Toda: Tetrahedron Letters, **1966**, 3663.
3) R.A. Massy-Westropp, G.D. Reynolds, T.M. Spotswood: Tetrahedron Letters, **1966**, 1939.

compounds of terpenoid origin. Along with those nor-sesquiterpenoids, we have isolated a new sesquiterpene hydrocarbon. In this paper, the evidences for its structural assignment are described together with the identification of two other compounds, α-costal[4,5] (or sesquibenihial) and a sesquiterpene alcohol, so-called cadinenol,[6,7] whose structure has not been established yet.



I II : R=CHO III : R=CH_2OH IV

Fig. 1.

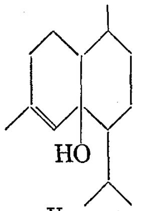
The hydrocarbon (I), $C_{15}H_{24}$ (mol. wt. by mass spectrum), colorless oil, $[\alpha]_D^{14}$ +32.05° (MeOH), was isolated by column and gas chromatography from the hydrocarbon part of the essential oil of the Benihi tree. Spectral data for I are as follows: UV, end absorption only; IR (neat), 3080, 1640, 1370 and 887 cm^{-1}; NMR in CCl_4, 8.97 (3H, s, -C-$\underline{CH_3}$), 8.43 (3H, broad s, -C=C-$\underline{CH_3}$), 8.30 (3H, t, J=0.9 c.p.s. CH_2=C-$\underline{CH_3}$) and 5.38 (2H, m, $\underline{CH_2}$=C-CH_3) τ. The presence of one tertiary methyl group and an isopropenyl group in I, and the known occurrence of eudalene and cadalene type sesquiterpenes, but not other types, in the Benihi tree,[8~10] lead to the conclusion that the structure of I is represented by bicyclo[4.4.0]-4,9-dimethyl-6-isopropenyldecene-4.[11] Naves has reported that the isomeric hydrocarbon prepared by acid treatment of α-selinene corresponds to I and has idenified this isomer with β-cyperene.[12] Furthermore, the same structure was assigned to the sesquiterpene called cyperene-2[13] (or β-cyperene). However, Šorm, and his cowokers have pointed out that cyperene-2 is actually identical with β-selinene.[14] To avoid the confusion of trivial names for the selinenes,[12~14] the authors suggest that the name "selina-4,11-diene" should be used for this sesquiterpene hydrocarbon.

A sesquiterpene aldehyde (II), $C_{15}H_{22}O$ (2,4-dinitrophenylhydrazone, m.p. 182°, $C_{21}H_{26}O_4N_4$), was also isolated; it has the following spectroscopic properties: UV, λ_{max}^{MeOH} 217 mμ (log ε 3.95); IR (neat), 3090, 2710, 1690, 1645, 1380, 940, 910 and 885 cm^{-1}; NMR in

4) *a*) V. Benesova, V. Herout, F. Šorm: Coll. Czech. Chem. Comm., **24**, 2365 (1959). *b*) A.S. Bawdekar, G.R. Kelkar, Tetrahedron, **21**, 1521 (1965).
5) Independently, the isolation of a mixture of α- and β-costal from *Thujopsis dolabrata* Sieb. et Zucc. has been reported by S. Itô, K. Endo, H. Honma, K. Ohta: Tetrahedron Letters, **1965**, 3777.
6) *a*) J. B-Son Bredenberg: Acta Chem. Scand., **11**, 98 (1957). *b*) M. Horah, O. Motl, J. Pliva, F. Šorm: "Die Terpene Sammlung der Spektren und Physikalischen Konstanten," 1960, Akademie Verlag, Berlin.
7) Y. Hirose and T. Nakatsuka have reported the properties of the alcohol obtained from *Juniperus rigida* Sieb. et Zucc. at "the 8th symposium of terpene, essential oil and perfume chemistry" by the Chemical Society of Japan, at Sendai, in Oct., 1964; abstract paper, pp. 181~184.
8) K. Kafuku, N. Ichikawa: Nippon Kagaku Zasshi, **52**, 222 (1932), **54**, 1011 (1933).
9) E. Sebe: *Ibid.*, **59**, 1285 (1938); **62**, 22 (1941); **64**, 909 (1953).
10) S. Katsura: *Ibid.*, **63**, 1460, 1465, 1470, 1477, 1480 (1942).
11) This compound was synthesized by Dr. Nagahama and his colleagues at Kyushu Univ., and IR and NMR spectra of I and the synthetic compound were identical: personal communication from Dr. Nagahama to Prof. Ito to whom the authors express their thanks for this information about Dr. Nagahama's work.
12) Y-R. Naves: Bull. chim. soc. France, **1956**, 292.
13) *a*) P.T. Narasimhan, R. Senich: Proc. Indian Acad. Aci., **43A**, 156 (1956); C.A., **51**, 318 (1957). *b*) R.N. Senic: Glasnik Sumarskog. Fak. Univ. Beograd, **17**, 829 (1959); C.A., **58**, 3462 (1963).
14) B. Triviedi, O. Motl, V. Herout, F. Šorm: Coll. Czech. Chem. Comm., **29**, 1675 (1964).

CCl_4, 9.25 (3H, s, $-\overset{|}{\underset{|}{C}}-\underline{CH_3}$), 5.63 and 5.34 (1H each, m, $-\overset{|}{C}=\underline{CH_2}$), 4.09 and 3.79 (1H each, broad s, $CHO-\overset{|}{C}=\underline{CH_2}$), and 0.52 (1H, s, $\underline{CHO}-\overset{|}{C}=CH_2$) τ. The above data suggest that II has the structure shown in Fig. 1; this was established by oxidation of sesquibenihiol[10] (or costol)[15] (III) with active manganese dioxide to afford an aldehyde whose IR and NMR spectra were identical with those of II. This is the fiirst reported occurrence of II in nature.[5]

The new alcohol (IV), $C_{15}H_{26}O$, m.p. 75°, $[\alpha]_D^7$ +5.02° (MeOH), was identified with so-called cadinenol by comparison of its spectral data with those reported by Šorm and his colleagues,[6] and by Hirose and Nakatsuka.[7] This alcohol has also been obtained from *Torreya nucifera* Sieb. et Zucc.[16] and *Schizandra nigra* Maxim.[17] by Hirose and his coworkers, and from *Thujopsis dolabrata* Sieb. et Zucc. by Endo.[18] Presumably, the distribution of this alcohol in nature is fairly common. Structure IV is proposed for the alcohol on the basis of the following evidence: UV, end absorption only; IR (KBr pellet), 3370, 1670, 1390, 1385, 1365, 1075, 1023, 918, 888 and 851 cm^{-1}; NMR in CCl_4, 9.19 (d, J=7.3 c.p.s., isopropyl methyl), 9.13 (d, J=7.3 c.p.s., isopropyl methyl), 9.09 (d, J=6.0 c.p.s., $H-\overset{|}{\underset{|}{C}}-\underline{CH_3}$), 8.34 (broad s, $-CH=\overset{|}{C}-\underline{CH_3}$) and 4.62 (1H, m, $-\underline{CH}=\overset{|}{C}-CH_3$) τ. Dehydrogenation of IV gave cadalene,[7] therefore IV is a cadinane type sesquiterpene alcohol having one double bond with one vinyl proton. However, IV does not give cadinene dihydrochloride. Since the alcohol is resistant to chromium trioxide oxidation in pyridine and the dihydro-derivative of IV shows a new C-O stretching band at 1135 cm^{-1} with disappearance of the band at 1075 cm^{-1} in its IR spectrum, the alcohol group of IV is tertiary and allylic. Furthermore, mild acid treatment of the alcohol afforded conjugate diene hydrocarbons, and main product ($C_{15}H_{24}$, by mass spectrum) possesses following spectroscopic properties: IR, 1635, 1625 cm^{-1}; UV, 239 mμ; namely, cadina-1,9-diene. Those facts lead to the conclusion that the structure of the alcohol is represented by formula IV or V (Fig. 2). Ozonolysis of the alcohol gave acetaldehyde,[7] suggesting that formula IV is more favorable than V, since the ozonide of IV would form an α-hydroxymethyl ketone which could afford acetaldehyde whereas the ozonide of V could not. The name "cadinenol" should be changed to "cadin-9-en-1-ol."



V

Fig. 2.

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15) V. Benesova, V. Sykora, V. Herout, F. Šorm: Chem. & Ind., **1958**, 363.
16) T. Sakai, K. Nishimura, H. Chikamatsu, Y. Hirose: Bull. Chem. Soc. Japan, **36**, 1261 (1963).
17) K. Morikawa, K. Nishimura, Y. Hirose: Nippon Kagaku Zasshi, **87**, 591 (1966).
18) Endo isolated the alcohol as an oil, however its IR spectrum is identical with that of IV. K. Endo, D. Sc. thesis: Tohoku University, August, 1965.