The Composition of the Volatile Oil Obtained from the Leaves of Torreya nucifera and the Structure of Torreyol

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The volatile oil obtained from *Torreya nucifera Sieb. et Zucc.* was first examined by Shinozaki;[1] α-pinene, camphene, limonene (ca. 60%), cadinene, and a crystallin sesquiterpenic alcohol (m. p. 137~138°C), which was named torreyol, were found to be its components. The structure of torreyol was shown by Nishida and Uota[2] to be represented by formula I on the basis of the fact that torreyol gave cadinene dihydrochloride upon reaction with hydrogen chloride and yielded acetone

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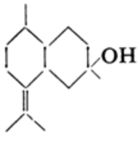
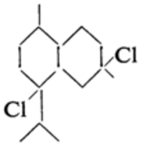
[1] E. Shinozaki, *J. Soc. Chem. Ind.* (*Kōgyō-Kwagaku Zasshi*), **25**, 768 (1922).

[2] K. Nishida and H. Uota, ibid., **43**, 150 (1940); **44**, 225 (1941).

by ozonolysis. The structure of cadinene dihydrochloride, at that time, was said by Ruzicka and Stoll[3] to be represented by structure II, and this formula was used in the study by Nishida and Uota. Later, this structure for cadinene dihydrochloride was found to be incorrect, and the revised structure, III, for it was suggested by Campbell and Soffer.[4] Therefore, the structure of torreyol also needed to be revised. Herout and his co-workers[5,6] reported that the physical properties of torreyol strikingly resemble those of δ-cadinol.



I



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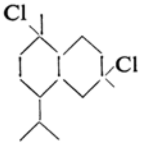

III

The purpose of this study is to elucidate the structure of torreyol and to obtain more precise data on the composition of the volatile oil.

Experimental

Two hundred and twenty-four grams of the volatile oil were obtained from 30.5 kg. of the leaves of *Torreya nucifera* by extraction with methanol, followed by steam distillation of the methanol extract. For the effectual recovery of torreyol and other sesquiterpene alcohols, the oil was treated by the following procedure. The oil was first separated by distillation under reduced pressure into a low-boiling fraction and a residual fraction containing mainly sesquiterpene alcohols. The latter was cooled, and the deposited crystals were collected. The same procedure was repeated on the filtrate until no crystalline material was deposited. The combined crystals were recrystallized from dilute ethanol. The oil recovered from the mother liquors of the recrystallization and the final filtrate were further separated by adsorption chromatogaphy on neutral alumina into three fractions, namely, a hydrocarbon fraction, a liquid sesquiterpene alcohol fraction, and a crystalline sesquiterpene alcohol fraction. By the above procedures, the original oil was separated into the following three fractions:

Fraction A: A low-boiling fraction separated by distillation, and a hydrocarbon fraction separated by adsorption chromatography on alumina. (209 g.)

Fraction B: A liquid sesquiterpene alcohol fraction separated by adsorption chromatography on alumina. (8.1 g.)

Fraction C: Crystalline sesquiterpene alcohol. (6.9 g.)

Fraction A.—Fraction A was further fractionated by distillation with Podbielniak's 13 mm. × 2ft. Heli-Grid column under reduced pressure, followed by adsorption chromatography on silica gel. Each fraction was analyzed by gas chromatography, spectroscopy, and chemical methods. The course of the fractional distillation is presented in Fig. 1.

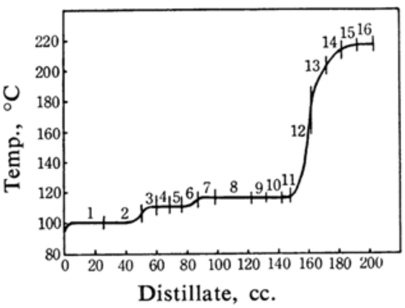

Fig. 1. The fractional distillation curve (50 mmHg).

The last fraction (fraction 17, 6 cc.) was recovered from the final residue by steam distillation.

Fractions 1 and 2 consisted only of α-pinene.

Fraction 3 was a mixture of hydrocarbons, which the infrared spectrum showed to contain myrcene. The myrcene was removed from the mixture as a maleic acid adduct. By adsorption chromatography of the unreacted portion, α-pinene, 3-carene, limonene, and γ-terpinene were isolated.

Fractions 4 to 6 contained limonene and myrcene.

Fractions 7 to 11 consisted only of limonene.

Fraction 12, the wide boiling range fraction, was a mixture of hydrocarbons and oxygen-containing compounds. The major constituents of this fraction were limonene and terpinolene. Minute amounts of linalool, terpinen-4-ol, citronellol, phenylethyl acetate and methyl salicylate were also found to be present by chromatographic separation.

Fractions 13 and 14 were complicated mixtures of hydrocarbons judged by gas chromatographic analysis to consist of at least nine hydrocarbons. However, it was so difficult to separate them by adsorption chromatography that only δ-cadinene, γ-cadinene, β-elemene, and two unknown sesquiterpene hydrocarbons could be isolated. Besides, fraction 13 contained small amounts of citronellol, geraniol and an unidentified carbonyl compound.

Fractions 15 to 17 consisted of relatively pure δ-cadinene.

Fraction B.—Fraction B, the liquid sesquiterpene alcohol fraction separated by adsorption chromatography on neutral alumina, was percolated again through a silica gel column. It contained nerolidol, two sesquiterpene alcohols, and an unidentified aromatic carbonyl compound.

One of the sesquiterpenic alcohols seemed to be identical with the so-called "cadinenol" isolated by Herout and his co-workers[5,7] from Juniper berry oil. The structure of cadinenol has not yet been

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[3] L. Ruzicka and M. Sotll, *Helv. Chim. Acta*, **7**, 94 (1924).

[4] W. P. Campbell and M. D. Soffer, *J. Am. Chem. Soc.*, **64**, 417 (1942).

[5] V. Herout and V. Sykora, *Tetrahedron*, **4**, 246 (1958).

[6] V. A. Pentegova, O. Motl and V. Herout, *Doklady Acad. Nauk SSSR*, **138**, 850 (1961).

[7] J. Pliva, M. Horak, V. Herout and F. Sorm, "Die Terpene. Der Spektrum und phys. Konstanten. Teil I. Sesquiterpene," Akademie-Verlag, Berilin (1960).

established. The infrared spectrum and the retention time on the gas chromatography of the alcohol isolated here were both identical with those of cadinenol, although the crystallization of the isolated alcohol was not effected by the seeding of an authentic sample of cadinenol. By referring to the values of the optical rotation of cadinenol ($[\alpha]_D$ $-89°$) and the isolated alcohol ($[\alpha]_D$ $+69°$), it was concluded that the isolated alcohol was an optical antipode of (−)-cadinenol obtained from Juniper berry oil.

TABLE I. THE COMPOSITION OF THE VOLATILE OIL.

Compound	%
Iimonene	41.4
α-Pinene	23.0
Myrcene	6.8
Terpinolene	0.7
3-Carene	0.3
γ-Terpinene	0.1
Citronellol	0.7
Terpinen-4-ol	0.4
α-Terpineol	0.3
Linalool	+
Geraniol	+
Methyl salicylate	0.2
Phenylethyl acetate	0.1
Unidentified carbonyl compound	0.1
δ-Cadinene	13.6
γ-Cadinene	2.0
β-Clemene	0.8
Sesquiterpene hydrocarbon I	1.0
Sesquiterpene hydrocarbon II	0.8
Torreyol (now δ-cadinol)	3.1
Cadinenol	1.2
Nerolidol	0.6
Sesquiterpene alcohol	1.0
Sesquiterpene hydrocarbon mixture	2.5
Unidentified carbonyl compound I	0.3
Unidentified carbonyl compouod II	0.2

The other sesquiterpene alcohol was difficult to separate from cadinenol, and its ultimated purity did not exceed 60%. The infrared spectrum of this compound was not identical with that of any known sesquiterpene alcohol, and further study was abandoned because there was an insufficient quantity of it.

Fraction C.—Fraction C was almost pure torreyol; m. p. 138∼139°C. Sublimation and recrystallization from 50% ethanol afforded pure torreyol; m. p. 139.5∼140.5°C, $[\alpha]^{18}_{D}$ 118.6° (*c* 2.075, ethanol).

The physical constants of the torreyols reported previously were m. p. 137∼138°C[1] and 141∼142°C[2], and $[\alpha]_D$ +99°19′[1] and +107°13′[2].

The findings on the composition of the volatile oil are summarized in Table I.

The Structure of Torreyol

Upon treatment with hydrogen chloride in dioxane-water, torreyol gave cadinene dihydrochloride; m. p. 119°C, $[\alpha]^{14}_{D}$ +40.8° (*c* 0.735, ethyl acetate). On the basis of the value of the optical rotation, the identity of the infrared spectrum, and the depression of the mixed melting point with (−)-cadinene dihydrochloride (m. p. 117∼118°C, $[\alpha]^{14}_{D}$ −40.7°), it can be said that the dihydrochloride of torreyol is undoubtedly (+)-cadinene dihydrochloride.

The oxidation of torreyol with potassium permanganate yielded a dihydroxy-ketone (m. p. 143∼144°C).[8] No acetone was detected by the ozonization of torreyol. These findings prove the previously suggested. Formula I for torreyol to be untenable; on the other hand, by a direct comparison of the mixed melting point and the infrared spectrum with an authentic sample,[9] torreyol was proved to be identical with (+)-δ-cadinol. It was an optical antipode of pilgerol[10] isolated from the oil of *Pilgerodendron uniferum* by Erdtman.[11]

TABLE II. THE PHYSICAL CONSTANTS OF δ-CADINOL

Name	M. p., °C	α_D	Source	Ref.
δ-Cadinol	139 ∼140	−109	*Juniperus communis*	5
Albicaulol	138 ∼139	−102.3*1	*Pinus albicaulis*	8
Pilgerol	140 ∼141	−107	*Pilgerodendron uniferum*	10
Cedrelanol	139 ∼140	−106	*Cedrela odorata Brasilensis*	12
δ-Cadinol	141	+118.4*2	*Pinus sibirica*	6, 13
Sesquigoyol	135.5	+ 99.5*2	*Pinus pentaphylla*	14
Torreyol	139.5∼140.5	+118.6*3	*Torreya nucifera*	

*1 at 23°C *2 at 20°C *3 at 18°C

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[8] W. G. Dauben, B. Weinstein, P. Lim and A. B. Anderson, *Tetrahedron*, **15**, 217 (1961).

[9] V. Herout, private communication.

[10] H. Erdtman, Z. Telechowicz and and F. G. Toploss, *Acta Chem. Scand.*, **1956**, 1563.

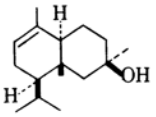
[11] H. Erdtman, private communication.

[12] G. Chiurdoglu, R. R. Smolders and A. Soquet, *Bull. soc. chim. Belg.*, **70**, 468 (1961).

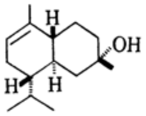
[13] V. A. Pentegova, O. Motl and V. Herout, *Collect. Czechoslov. Chem. Commun.*, **26**, 1362 (1961).

[14] Y. Sebe, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaishi*), **61**, 1269 (1940).

The structure of (−)-δ-cadinol has to be represented by formula IV, proposed by Dauben and his co-workers;[8] therefore the structure of (+)-δ-cadinol has to be shown by formula V.



IV



V

The physical constants of δ-cadinol obtained from various sources are shown in Table II.

Summary

It was found that the volatile oil from the leaves of *Torreya nucifera* contains limonene, 41.4%; α-pinene, 23.0%; myrcene, 6.8; terpinolene, 0.7%; 3-carene, 0.3%; γ-terpinene, 0.1%; citronellol, 0.7%; terpinen-4-ol, 0.4%; α-terpineol, 0.3%; methyl salicylate, 0.2%; phenylethyl acetate, 0.1%; δ-cadinene, 13.6%; γ-cadinene, 2.0%; β-elemene, 0.8%; torreyol (δ-cadinol), 3.1%; (+)-cadinenol, 1.2%; nerolidol, 0.6%; small amounts of linalool and geraniol; two unknown sesquiterpenic hydrocarbons, 1.8%; an unknown sesquiterpene alcohol, 1.0%, and three unidentified carbonyl compounds.

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