

THE CHEMISTRY OF CADINENES AND CADINOLS

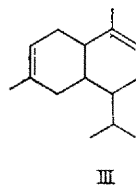
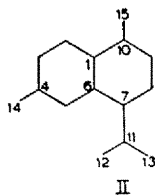
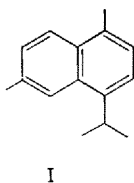
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Abstract—A number of sesquiterpenoid hydrocarbons, the cadinenes, and tertiary alcohols, the cadinols, have been isolated in a pure state in these Laboratories during the past few years. Their constitution and absolute configuration have been established. This review is intended to be a brief survey of the history of these compounds as well as a summary of our results.

THE sesquiterpenoid hydrocarbons $C_{15}H_{24}$ (cadinenes) and tertiary alcohols $C_{15}H_{28}O$ (cadinols) have long been known.^{1,2,3,4} Soubeiran and Capitaine⁵ prepared crystalline cadinene hydrochloride from cubeba oil. On account of the ready formation of this derivative, cadinene was detected in a number of ethereal oils.² Wallach⁶ was the first to use the name cadinen for these hydrocarbons. A number of investigators, particularly Semmler and his co-workers, examined the chemistry of the cadinenes, but, the most important contribution to the elucidation of their structure was made by Ruzicka and his collaborators,⁷ who dehydrogenated cadinene to cadalene (I) and proved its structure. The location of the double bonds in the cadinene skeleton (II) was achieved by the elegant work of Campbell and Soffer⁸ who showed that the so-called β -cadinene which could be re-generated from cadinene hydrochloride has structure (III).



Semmler and Jonas⁹ isolated the first cadinol from galbanum oil, and later, a number of other cadinols yielding cadinene dihydrochloride were isolated (cf. ref. 1-4). This indicates that the cadinols possess the same carbon skeleton as cadinene, and that the double bond and the hydroxyl group must be attached to the same carbon atoms.

Since most of the cadinols and all the cadinenes which have been described were obtained as liquids (by fractional distillation without the use of efficient columns), it is evident that they must have been mixtures. These could be characterised either

¹ J. Simonsen, D. H. R. Barton and L. N. Owen, *The Terpenes* Vol. III. Cambridge University Press (1952).

² *Elsevier's Encyclopedia of Organic Chemistry* (Edited by F. Radt) Ser. III, Vol. 12B, pp. 176-188, 322-324 and 1434-1437.

³ A. J. Haagen-Smit, *Fortschr. Chem. Org. Naturstoffe* **12**, 1 (1955).

⁴ D. H. R. Barton, *Quart. Rev.* **11**, 189 (1957).

⁵ E. Soubeiran and H. Capitaine, *Liebigs Ann.* **34**, 323 (1840).

⁶ O. Wallach, *Liebigs Ann.* **271**, 297 (1892).

⁷ L. Ruzicka, *Über Konstitution und Zusammenhänge in der Sesquiterpenreihe*. Bornträger, Berlin (1928).

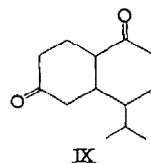
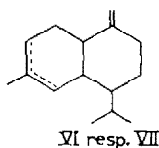
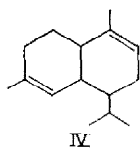
⁸ W. P. Campbell and M. D. Soffer, *J. Amer. Chem. Soc.* **64**, 417 (1942).

⁹ F. W. Semmler and K. G. Jonas, *Ber. Dtsch. Chem. Ges.* **47**, 2073 (1914).

by the formation of cadinene dihydrochloride (or dihydrobromide) or by dehydrogenation to cadalene which forms a number of crystalline derivatives. In order to distinguish the different cadinenes and cadinols the prefixes *d*- and *l*- indicating only the direction of the optical rotation, were used at first. These compounds were not true antipodes as was sometimes claimed in the literature¹ since both dextro- and laevo-rotatory cadinenes and cadinols afforded only (—)-cadinene-dihydrochloride or -dihydrobromide. Ruzicka and Stoll¹⁰ introduced a better system of notation based on Greek letters as prefixes for compounds of the cadinane series which differed in the position of the double bonds. Recently we proposed a rational nomenclature derived from the root *cadin*-¹¹ for cadinane derivatives having skeleton (II). The numbering of the skeleton is based on the principle formulated by Barton and his collaborators.¹² Its advantages lie in the fact that it relates the cadinane carbon atoms with those of other sesquiterpenoid derivatives, e.g. those of selinane (= eudesmane) and guaiane. This nomenclature is not limited to substances which yield cadinene dihydrochloride, but is applicable to all compounds possessing the cadinane skeleton.

In recent years better techniques for the isolation and identification of cadinenes and cadinols have become available, permitting the isolation of a number of cadinenes and cadinols in a relatively pure state. Table 1 summarises the physical constants of the cadinenes thus obtained.

Substance (IV) (α -cadinene) is not known, although Briasco and Murray assigned this structure to a hydrocarbon from *Dacrydium Colensoi*¹³ but no proof of this formulation was provided.* A β -cadinene ($[\alpha]_D^{20} -130^{\circ}$) obtained by the dehydrohalogenation of (—)-cadinene dihydrochloride has been described in the literature; it is, in fact, a mixture of cadinenes. Campbell and Soffer⁸ showed that the principal component of the mixture was the hydrocarbon (III). We have recently obtained a sample of very pure β -cadinene with a high optical rotation ($[\alpha]_D^{20} -251^{\circ}$) by fractionation through an efficient column.³⁷ In the course of this distillation was also separated a small amount of a hydrocarbon with a methylene group. Its physical constants d_4^{20} 0.9298, n_D^{20} 1.5099, $[\alpha]_D^{20} -13.3^{\circ}$ suggest that it may be identical with the so-called γ_1 -cadinene described by Bhattacharyya and his co-workers^{15,16} (see below).



Kafuku and his collaborators¹⁷ isolated a hydrocarbon from oil of citronella which they termed γ -cadinene. This hydrocarbon was separated¹⁴ in a comparatively

* The authors reversed the terms α - and β -cadinene contrary to Ruzicka's original proposal;¹⁰ cf. also Herout *et al.*¹⁴

¹⁰ L. Ruzicka and M. Stoll, *Helv. Chim. Acta* 7, 84 (1924).

¹¹ O. Motl, V. Šýkora, V. Herout and F. Šorm, *Chem. Listy* 52, 316 (1958).

¹² D. H. R. Barton, P. de Mayo and M. Shafiq, *J. Chem. Soc.* 929 (1957).

¹³ J. D. Briasco and J. Murray, *J. Appl. Chem.* 2, 187 (1952).

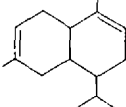
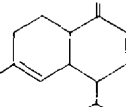
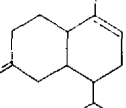
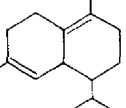
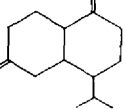
¹⁴ V. Herout, T. Kološ and J. Plíva, *Chem. Listy* 47, 440 (1953); *Coll. Trav. Chim. Tchécosl.* 18, 886 (1953).

¹⁵ K. K. Chakravarti and S. C. Bhattacharyya, *Perf. & Ess. Oil Rec.* 365 (1955).

¹⁶ B. B. Ghatgey, R. K. Razdan and S. C. Bhattacharyya, *Perf. & Ess. Oil Rec.* 157 (1956).

¹⁷ K. Kafuku, T. Ikeda and Y. Fujita, *J. Chem. Soc. Japan* 53, 636 (1932); *Chem. Abstr.* 27, 280 (1933).

TABLE I. SURVEY OF KNOWN CADINENES^a

Name ^b	No.	Formula	d_4^{20}	n_D^{20}	$[\alpha]_D$	Infra-red frequency of double bond	Ref
β -Cadinene Cadina-3,9-diene	III		0.9239	1.5059	-251	790,812, 822 cm ^{-1c}	37
γ -Cadinene Cadina-4,10 (15)-diene	VII		0.9125	1.5075	+148°	794,836 cm ^{-1c} 890 cm ^{-1d}	14
γ_1 -Cadinene Cadina-4(14), 9-diene	V		—	<i>1.5155^e</i>	<i>-19°^f</i>		16
δ -Cadinene Cadina-4,10 (1)-diene	VIII		0.9175	1.5086	+94°	836 cm ^{-1c}	14
ϵ -Cadinene Cadina-4(14),10 (15)-diene	X		0.9107	1.5038	+47°	890 cm ^{-1d}	20

^a The data obtained in these Laboratories are printed in ordinary type, those of other authors are *italicised*.

^b The trivial names are given first, followed by the systematic names based on the nomenclature introduced by us.^{11,16}

^c Frequencies of trisubstituted double bonds.

^d Frequency of methylene double bond.

^e At 26.5°.

^f The original paper records this value as "optical rotation".

pure state ($[\alpha]_D^{20} +148^\circ$) from the same oil by fractional distillation and chromatography on alumina. The infra-red spectrum of the γ -cadinene obtained had a distinct band due to a methylene group and bands due to a trisubstituted double bond (see Table 1). In agreement with this observation the compound yielded the theoretical amount of formaldehyde (corresponding to one methylene group¹⁸ on quantitative ozonolysis); and cadinene dihydrochloride in high yield.

Chakravarti and Bhattacharyya¹⁵ have recently isolated a laevorotatory cadinene from Malabar lemon grass oil. Ghatgey, Razdan and Bhattacharyya¹⁶ established structure (V) for this compound and named it γ_1 -cadinene. Dev and Guha¹⁹ demonstrated the presence of the same hydrocarbon in the sesquiterpenoid fraction from the oil of *Hardwickia pinnata*. In view of the fact that our γ -cadinene is not identical with γ_1 -cadinene as shown by the marked difference in their optical rotations, we were able to postulate that the methylene group in γ -cadinene is attached to C₍₁₀₎ in the cadinane skeleton and that it must therefore have structure (VI) or (VII). Conclusive evidence for structure (VII) was obtained by the pyrolysis of α -cadinol *p*-nitrobenzoate (see below) to γ -cadinene.¹⁸

Another dextrorotatory cadinene, which affords (—)-cadinene dihydrochloride in high yield, was isolated from a number of essential oils (oil of ylang-ylang,²⁰ citronella,¹⁴ sweet-flag,²¹ oil of false cubebs²²). This was termed δ -cadinene,²³ and its infra-red spectrum displayed absorption bands due to double bonds (cf. Table 1) indicating the absence of a methylene group and showing that the two double bonds are located in positions different from those in β -cadinene. On the basis of these facts structure (VIII) was assigned²³ to δ -cadinene. Corroborating evidence for this structure was obtained from the observation that the two epoxide groups in δ -cadinene dioxide are considerably less reactive²⁴ than the epoxide groups in β -cadinene dioxide.⁸

The so-called ϵ -cadinene²⁰ was isolated from oil of ylang-ylang. This substance also affords (—)-cadinene dihydrochloride. Ozonisation gives rise to two molecules of formaldehyde and the crystalline diketone (IX),²⁴ indicating that both double bonds must be present as methylene groups (see also infra-red absorption bands, Table 1). ϵ -Cadinene must therefore have structure (X). Dev and Guha¹⁹ also demonstrated the presence of ϵ -cadinene in the mixture of cadinenes obtained from *Hardwickia pinnata*.

The isolation of β , γ , γ_1 , δ and ϵ -cadinene proves the existence of five positional isomers of cadinene, although nine hydrocarbons, having double bonds attached to C₍₄₎ and C₍₁₀₎ and being able to yield (—)-cadinene dihydrochloride, are theoretically possible.

The cadinols isolated by earlier workers were generally obtained as liquids whose individuality was not rigorously established, (for a review see, e.g., refs. 1, 2). Only in recent times have some cadinols been obtained in a crystalline state (see Table 2).

¹⁸ V. Šýkora and V. Herout, *Chem. Listy* In press.

¹⁹ S. Dev and P. C. Guha, *J. Indian Chem. Soc.* **26**, 263 (1949).

²⁰ V. Herout and D. J. Dimitrov, *Chem. Listy* **46**, 432 (1952).

²¹ F. Šorm, M. Holub, V. Šýkora, J. Mleziva, M. Steribl, J. Plíva, B. Schneider and V. Herout, *Chem. Listy* **46**, 554 (1952); *Coll. Trav. Chim. Tchécosl.* **18**, 512 (1953).

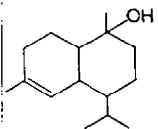
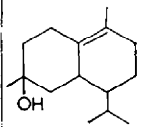
²² F. Vonášek. Private communication.

²³ J. Plíva, V. Herout, B. Schneider and F. Šorm, *Chem. Listy* **46**, 410 (1952); *Coll. Trav. Chim. Tchécosl.* **18**, 500 (1953).

²⁴ V. Herout, F. Šantavý, *Chem. Listy* **47**, 70 (1953); *Coll. Trav. Chim. Tchécosl.* **19**, 118 (1954).

The first crystalline cadinol was obtained by Plattner and Márkus²⁵ from Javanese citronella oil. The same alcohol was isolated by Kritchevski and Anderson²⁶ from *Chamecyparis lawsoniana* Stump and Heartwood, and by workers in this Laboratory,¹¹

TABLE 2. SURVEY OF KNOWN CRYSTALLINE CADINOLS^a

Name ^b	No.	Formula	M.p.	$[\alpha]_D$	Infra-red frequency of double bond	Lit.
α -Cadinol Cadina-4-en-10-ol	XI		72.5 74.5 <i>74.8-75.4</i>	-39.4 -47 -38.5	815 cm ^{-1c}	25 11 26
δ -Cadinol ^d Cadina-1(10)-en-4-ol	XV		139-140 <i>138.5-139</i>	-109 -107		11 28
Cadinol of unknown constitution			78.5-79	-89	831 cm ^{-1c}	11
Sesquigoyol ^e			135.5	+99.5	—	29

^a The data obtained in these Laboratories are printed in ordinary type; those of other authors are *italicised*.

^b The trivial names are given first followed by the systematic names based on the nomenclature introduced by us.^{11,26}

^c Frequency of trisubstituted double bond.

^d A laevorotatory cadinol of m.p. 137.5-138.5°, which was isolated from *Dictyopteris divaricata*,²⁷ might be identical with δ -cadinol.

^e Affords ()-cadinene dihydrochloride.

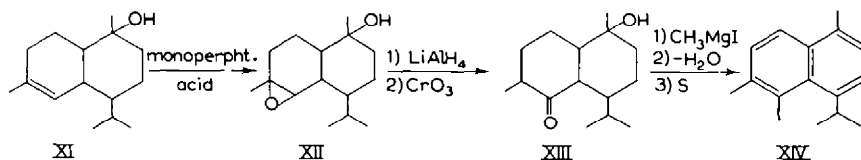
from *Juniperus communis* L. We have recently been able to elucidate its structure by converting it into the keto-alcohol (XIII) via the epoxy-alcohol (XII). Methylation of the keto-alcohol (XIII) by means of Grignard reagent followed by dehydrogenation afforded 1:5:6-trimethyl-4-isopropyl-naphthalene (XIV). This reaction sequence

²⁵ P. A. Plattner and R. Márkus, *Helv. Chim. Acta* **25**, 1674 (1942).

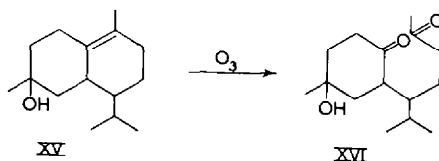
²⁶ G. Kritchevsky and A. B. Anderson, *J. Amer. Pharm. Assoc.* **44**, 535 (1955).

²⁷ M. Takaoka and Y. Ando, *J. Chem. Soc. Japan, Pure Chem. Sect.* **72**, 999 (1951); *Chem. Abstr.* **46**, 9261 (1952).

indicates structure (XI) for this alcohol and hence the name α -cadinol. (cf. ref. 1). Soffer and his collaborators³⁰ have reached the same conclusion independently.



Erdtman *et al.* isolated a crystalline cadinol from the conifer *Pilgerodendron wififerum* (D. Don) Florin which they termed pilgerol.²⁸ The same alcohol was isolated in this Laboratory from oil of juniper berries and, more recently, from oil of false cubebs.²² Contrary to the results of Erdtman *et al.* we found that the infra-red spectrum of this alcohol does not contain bands characteristic of a trisubstituted double bond nor of a methylene group. This pointed to the fact that the double bond is tetrasubstituted and that the alcohol must therefore have structure (XV) and be termed δ -cadinol. This was confirmed¹¹ by the ozonisation of δ -cadinol to a compound $C_{15}H_{26}O_3$, whose infra-red spectrum exhibited an intense band at 1708 cm^{-1} due to a keto group and a band at 3400 cm^{-1} due to a hydroxyl group. The above compound does not contain an aldehyde group in accordance with the postulated structure for δ -cadinol. The product of ozonolysis can thus be formulated as (XVI).



Another crystalline cadinol of m.p. $78.5\text{--}79^\circ$ was also isolated from oil of juniper berries.¹¹ Its structure is being investigated at present.

Mention should also be made of the so-called taiwanol³¹ (from *Taiwania cryptomerioides* Hayata) which is not crystalline but affords a solid phenylurethane of m.p. $134\text{--}135^\circ$. The alcohol torreyol³² (from *Torreya nucifera* S. et Z.; m.p. $139\text{--}140^\circ$; $[\alpha]_D^{20} +107.1^\circ$) cannot be definitely regarded as a cadinol. Although the authors record that it affords cadinene dihydrochloride, this fact conflicts with the observation that acetone is formed from it on ozonolysis. The physical constants of torreyol are strikingly close to those of the so-called sesquigoyol (from *Pinus pentaphylla*, m.p. 135.5° , $[\alpha]_D^{20} +99.5^\circ$) but the latter affords (+)-cadinene dihydrochloride.²⁹

It may thus be said that only three cadinols have been firmly established out of the twelve theoretically possible forms which can give rise to (–)-cadinene dihydrochloride.

So far, only Ruzicka and his collaborators have studied the stereochemistry of cadinane derivatives. By comparing the physical constants of a number of substituted decalins the above authors concluded that the fusion of the two rings in the cadinane

²⁸ H. Erdtman, Z. Pelchowicz and J. G. Topliss, *Acta Chem. Scand.* **10**, 1563 (1956).

²⁹ Y. Sebe, *J. Chem. Soc. Japan* **61**, 1269 (1940); *Chem. Abstr.* **37**, 4064 (1943).

³⁰ M. D. Soffer, M. Brey and J. Fournier, *Chem. & Ind.* **19**, (1958).

³¹ K. Kafuku and R. Kato, *Bull. Chem. Soc. Japan* **6**, 65 (1931); *Chem. Abstr.* **25**, 3125 (1931).

³² K. Nishida, H. Uota, *J. Soc. Chem. Ind. Japan*, Suppl. bind. **43**, 64 (1940); *Chem. Abstr.* **34**, 6936 (1940); *J. Soc. Chem. Ind. Japan*, Suppl. bind. **44**, 119 (1941); *Chem. Abstr.* **38**, 4262 (1944).

skeleton i cis¹, but, their method did not lead to the correct results as shown by the similar case of eudesmol.³³

Since cadinane derivatives afford the crystalline (—)-cadinene dihydrobromide (or dihydrochloride), physical rather than chemical methods seemed to be indicated for determining the relative configuration at all the asymmetric centres. Purely chemical methods do not appear to be practicable in the case of cadinane derivatives. Cadinene dihydrobromide is particularly suitable for X-ray diffraction measurements on account of the presence of the two heavy atoms in the molecule. The measurements were carried out at our suggestion by Hanic³⁴ who showed that it may be represented by formula (XVIIb) or its mirror image. Thus the two rings are trans-fused, the three alkyl groups are equatorial and the two halogen atoms are axial and lie on the same side of the molecule. The results of dipole moment measurements (cadinene dihydrochloride 4.06D, cadinene dihydrobromide 4.20D; Jehlicka and Reiser³⁵) are in accordance with this structure.

Hence all compounds affording (—)-cadinene dihydrobromide (or the corresponding dihydrochloride) must have the same configuration at C₍₁₎, C₍₆₎ and C₍₇₎ (see formula II) which are not involved in the formation of the derivative. It only remained to establish the absolute configuration of at least one of the asymmetric carbon atoms in order to elucidate the absolute configuration of all the centres of asymmetry.

For this reason the isolation of optically active isopropylsuccinic acid^{36,37} from the products of oxidative degradation of β-cadinene was attempted.

Paper chromatography by the method of Šanda, Procházka and Le Moal³⁸ permitted the detection of a C₇ carboxylic acid in the mixtures obtained by the oxidation of β-cadinene with various reagents. The same method was also employed as a check during the isolation and final stages of purification of isopropylsuccinic acid. Nitric acid was used for the degradation starting with either β-cadinene or its ozonolysis product. The isopropylsuccinic acid thus obtained was found to be D-(+)-isopropylsuccinic acid (XVIII).^{36,37*} Hence structure (XVIIa) and (XVIIb) could be assigned to cadinene dihydrochloride and dihydrobromide, respectively.

Evidence for the absolute configuration of cadinane derivatives was also obtained by a different method. Two crystalline ketones, which were isolated in the course of investigation¹¹ of the constitution of α-cadinol, were shown to have the absolute configuration represented by (XIX) and (XX). This was achieved by means of the method of rotatory dispersion curves which has recently been developed by Djerassi (cf. ref. 39, 40). Fig. 1 shows the dispersion curves of these ketones and of ketone (XXI) whose configuration has been established by Djerassi.^{41†} The rotatory dispersion

* We are indebted to Prof. A. Fredga, of the University of Uppsala, for kindly supplying a specimen for reference.

† We are indebted to Prof. C. D. Djerassi, of Wayne University, Detroit, for measuring the rotatory dispersion curves of our ketones and for supplying reference compounds prior to publication.

³³ R. Riniker, J. Kalvoda, D. Arigoni, A. Fürst, O. Jeger, A. M. Gold and R. B. Woodward, *J. Amer. Chem. Soc.* **76**, 313 (1954).

³⁴ F. Hanic, *Chem. Listy* **52**, 165 (1958).

³⁵ V. Jehlicka and A. Reiser, *Chem. Listy* in press.

³⁶ V. Herout and V. Šykora, *Chem. & Ind.* 130 (1958)

³⁷ V. Šykora, V. Herout and F. Šorm, *Chem. Listy* In press.

³⁸ V. Šanda, Z. Procházka and H. Le Moal, *Chem. Listy* In press.

³⁹ C. Djerassi, *Bull. Soc. Chim. Fr.* 741. (1957)

⁴⁰ C. Djerassi, R. Riniker and B. Riniker, *J. Amer. Chem. Soc.* **78**, 6362 (1956).

⁴¹ C. Djerassi and D. Marschall, *J. Amer. Chem. Soc.* **80**, In press.

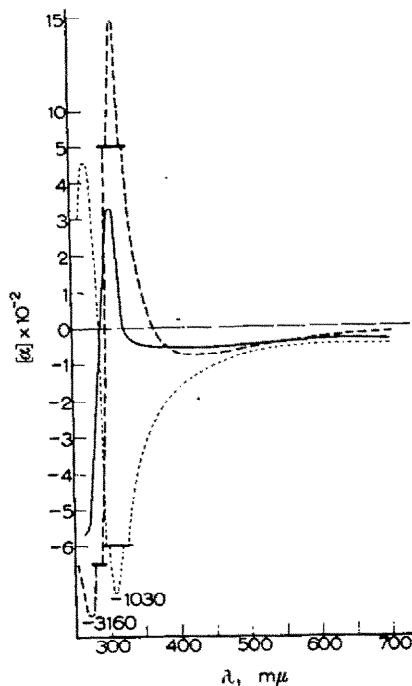
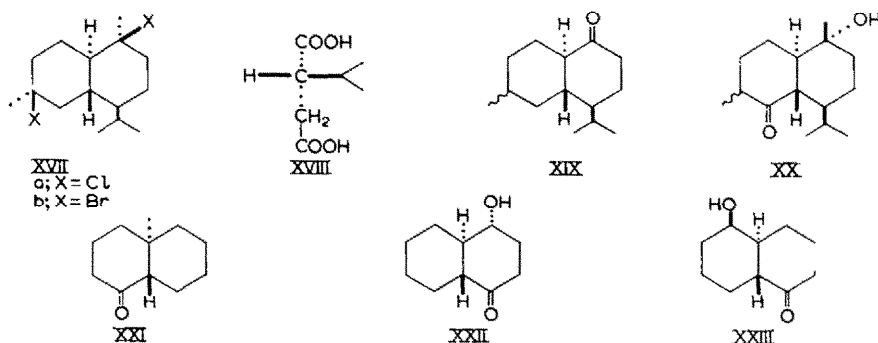


FIG. 1. Rotational dispersion curves.

10-desmethylcadinan-10-one (XIX; - - - -), cadinan-10-ol-5-one (XX; - · - · - ·), and *trans*-10-methyldecal-1-one (XXI; ———).

curves of the hydroxydecalones (XXII) and (XXIII), prepared by Prelog *et al.*^{42*} are in good agreement with our results.

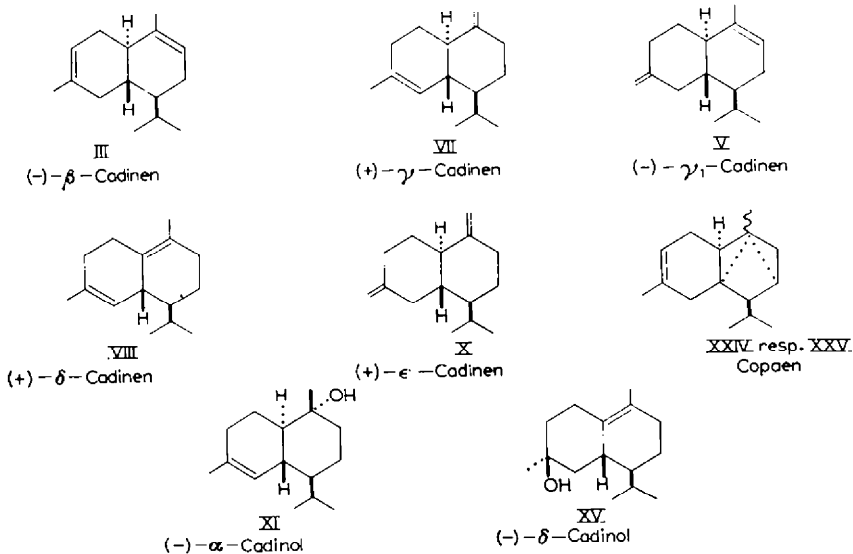


The above-mentioned findings permit the assignment of configuration to a number of other compounds. (see Table 3). The configuration of the hydroxyl groups of α -cadinol (XI) and δ -cadinol (XV) was deduced from the ease of esterification and, in the case of α -cadinol, also from the manner of dehydration.¹¹ The position of the

* We thank Prof. Prelog, E.T.H., Zurich, for kindly supplying this material prior to publication.

⁴² V. Prelog *et al.*, *Helv. Chim. Acta* 41, In press.

three-membered ring in the tricyclic hydrocarbon copaene⁴³ (XXIV or XXV), another compound which affords (—)-cadinene dihydrochloride, has not so far been established. The asymmetric centres at C₍₁₎ and C₍₇₎ must have the same absolute configuration as the corresponding carbon atoms in (—)-cadinene dihydrobromide.



Beside (—)-cadinene dihydrochloride, the (+)- and (\pm)-enantiomers^{2,45} are also known. (+)-Cadinene dihydrochloride was prepared from sesquigoyol²⁹ (see above) and from a number of cadinenes isolated from various plants.^{44–46} (cf. also ref. 2) The earliest data concerning the preparation of (+)-cadinene dihydrochloride⁴⁴ must be accepted with certain reservations in view of the low optical rotation of the material. It would be remarkable, from a biogenetic point of view, if it were proved that the same plant could produce different sesquiterpene enantiomers under different conditions.⁴⁵

A number of compounds having skeleton (I), which do not afford cadinene dihydrochloride, are known. They are termed *isocadinenes*² but their individuality is in doubt. *iso*-Zingiberene which was obtained from its dihydrochloride by regeneration, is the only compound which may be regarded as homogeneous; it has been assigned⁴⁷ structure (XXVI).* Sesquibeniene, which according to Katsura⁴⁹ has structure (XXVII), has also been investigated.

Hydrocarbons of molecular formula C₁₅H₂₂ and C₁₅H₂₀, which possess the cadinene skeleton, have been described. The former compound, calamene, was isolated from oil of sweet flag.^{1,2,21} Its structure (XXVIII) was elucidated in these Laboratories.⁵⁰

* The configuration at C₍₁₎ and C₍₁₀₎ is probably the same as that of zingiberene.⁴⁸

⁴³ L. H. Briggs and W. J. Taylor, *J. Chem. Soc.* 1338. (1947)

⁴⁴ M. E. Grimal, *C. R. Acad. Sci., Paris* 135, 1057 (1902).

⁴⁵ R. O. Hellyer and H. H. G. McKern, *Aust. J. Chem.* 9, 547 (1956).

⁴⁶ A. J. Birch, *J. Chem. Soc.* 715 (1953).

⁴⁷ M. D. Soffer, C. Steinhardt, G. Turner and M. E. Stebbins, *J. Amer. Chem. Soc.* 66, 1520 (1944).

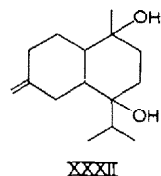
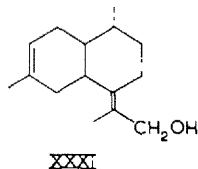
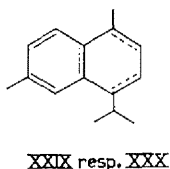
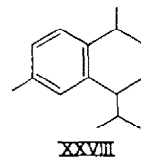
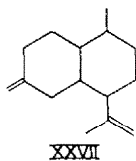
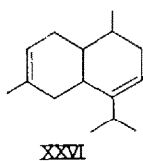
⁴⁸ D. Arigoni, O. Jeger, *Helv. Chim. Acta* 37, 881 (1954).

⁴⁹ S. Katsura, *J. Chem. Soc. Japan* 63, 1470 (1942).

⁵⁰ F. Šorm, K. Veres and V. Herout, *Chem. Listy* 46, 100 (1952).

The hydrocarbon calacorene, $C_{15}H_{20}$, was isolated from the same oil; and has structure (XXIX) or (XXX).⁵¹

The isocadinols $C_{15}H_{26}O$, which possess skeleton (I) but which do not afford cadinene dihydrochloride, include a crystalline alcohol of m.p. 75° , $[\alpha]_D^{20}$: $+3.7^\circ$ from Bulgarian juniper oil. Khusol, isolated from vetiver oil, has the same skeleton but a different molecular formula ($C_{15}H_{24}O$); Bhattacharyya *et al.*⁵² tentatively propose structure (XXXI) for it. Calameon, a sesquiterpenoid diol $C_{15}H_{24}O_2$, which has the skeleton (I), has been isolated from oil of calamus. It has structure (XXXII).⁵³



In this review we have attempted to survey the most important advances which have been made in this interesting group of sesquiterpenes. Even though the constitution and absolute configuration of a number of these compounds has been elucidated, a number of problems still await solution, particularly in connection with compounds having a cadinane skeleton and not yielding cadinene dihydrochloride.

⁵¹ O. Mottl, Private communication.

⁵² S. N. Dhingra, D. R. Dhingra and S. C. Bhattacharyya, *Perf. & Ess. Oil Rec.* 350 (1956).

⁵³ W. Treibs, *Ber. Dtsch. Chem. Ges.* 82, 530 (1949).