
Terpenoids and Steroids- Volume 5

Specialist Periodical Reports

The Chemical Society

A Specialist Periodical Report

Terpenoids and Steroids

Volume 5

A Review of the Literature Published
between September 1973 and August 1974

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The Chemical Society

Burlington House, London, W1V 0BN

ISBN: 0 85186 296 9

ISSN: 0300-5992

Library of Congress Catalog Card No. 74-615720

Set in Times on Monophoto Filmsetter and printed offset by
J. W. Arrowsmith Ltd., Bristol, England

Made in Great Britain

Introduction

This Report covers the literature published between September 1973 and August 1974, except for the chapter on Steroid Synthesis, a topic omitted from Volume 4, which consequently reviews a two-year period from September 1972 to August 1974.

The tight-rope economics of producing these Reports have unfortunately forced us to abandon our plan to include occasional reviews, which we had hopefully begun in Volume 4. We do include a list of selected Reviews on Steroid Chemistry 1969—1974, to complement the Reviews on Terpenoid Chemistry that appeared in Volume 4, and also a classified list, which just eluded the economic axe, of Terpenoid Structures determined by *X*-Ray Analysis. As always, comments, criticisms, and suggestions for future volumes will be heartily welcomed.

K. H. OVERTON

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Part I

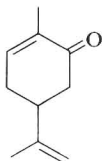
TERPENOIDS

There has been little increase in the volume of work published this year, but the space available for this Report is slightly reduced, so economy has been achieved in two ways. Papers not requiring any discussion, either because they are repetitive or because the minor point they make is evident from little more than the title, are placed at the end of each section. The number of formulae has been reduced, and more extensive use is made of names in the text. With these limitations, every effort has been made to quote all papers relevant to monoterpenoids.

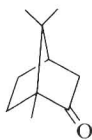
1 Physical Measurements: Spectra *etc.*; Chirality

Titanium tetrachloride is recommended as a useful shift reagent in assigning ^{13}C n.m.r. frequencies, particularly in $\alpha\beta$ -unsaturated ketones such as carvone (1), which has a shift of -5.83 Hz for the β -carbon frequency, compared with -1.51 Hz using $[\text{Eu}(\text{fod})_3]$.¹ The ^{13}C signals of the bridge methyl groups of camphor (2) (C-9 and C-10) have been assigned using another new shift reagent, tris-[4,4,4-trifluoro-1-(2-thienyl)-1,3-butadiene]europium(III),² and ^{13}C chemical shifts of substituted tricyclenes are discussed.³ The importance of non-axial symmetry in interpreting lanthanide-induced shifts in ketones has special relevance for monoterpenoids, and Newman discusses the case of camphor (2).⁴ Shifts induced by $[\text{Eu}(\text{dpm})_3]$ in saturated *o*- and *p*-menthones,⁵ and its effect on the rotation of the isopropyl group in menthone and menthol have been measured.⁶

Some well known mass spectra of monoterpenoid alcohols have been published again.⁷



(1)



(2)

¹ A. K. Bose, P. R. Srinivasan, and G. L. Trainor, *J. Amer. Chem. Soc.*, 1974, **96**, 3670; 9th International Symposium on the Chemistry of Natural Products, Ottawa, 1974, Abstracts 20B; A. K. Bose, personal communication.

² K. Beyer, *Org. Magn. Resonance*, 1974, **5**, 471.

³ E. Lippmaa, T. Pehk, and J. Paasivirta, *Org. Magn. Resonance*, 1973, **5**, 277.

⁴ R. H. Newman, *Tetrahedron*, 1974, **30**, 969.

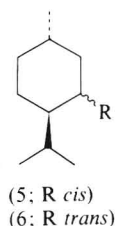
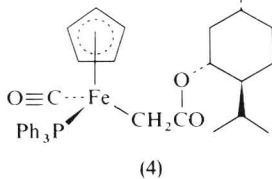
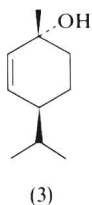
⁵ R. Enriquez, J. Taboada, I. Salazar, and E. Diaz, *Org. Magn. Resonance*, 1973, **5**, 291.

⁶ K. Yamada, S. Ishihara, and H. Iida, *Chem. Letters*, 1973, 549.

⁷ G. R. Rik and L. V. Kravchenko, *Vestnik Sel'skokhoz. Nauki (Moscow)*, 1973, 104 (*Chem. Abs.*, 1973, **79**, 70083).

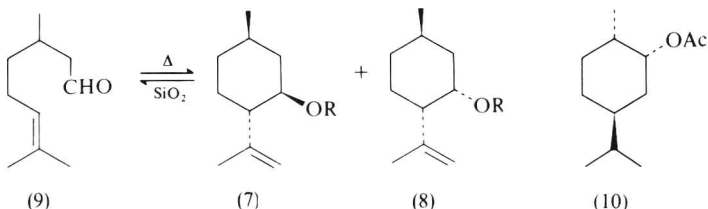
The adsorption on a mercury electrode of borneol and adamantan-1-ol has been compared with that of camphor because of similar polarographic behaviour.⁸

The chirality of alcohols, notably (–)-linalool, (–)-menthol, and *cis*-menth-2-enol (the name in the text is different), is rapidly established by measuring the c.d. of the complex with copper hexafluoroacetylacetonate.⁹ Photodecomposition of racemic camphor with circularly polarized light occurs enantiomerically, the optical purity of recovered camphor theoretically rising to 100% at the end of the reaction. After 99% destruction of the (±)-camphor, the remainder has 20% optical activity.¹⁰



Notable examples of the induction of asymmetry by complexing with monoterpenoids are the resolutions of the iron complex (4)¹¹ and a titanium¹² complex. The menthyl- (5; R = PPh₂) and neomenthyl- (6; R = PPh₂) diphenylphosphines are epimeric, chiral ligands, suitable for asymmetric syntheses.¹³ Another account has appeared of an attempt to induce asymmetry by cyclization of homogeranic (–)-menthyl ester.¹⁴

Various micro-organisms (*Trichoderma*, *Absidia*, etc.) hydrolyse some racemic acetates chirally; thus a mixture of (±)-isopulegyl acetate [(±)-(7; R = COMe)] and (±)-neoisopulegyl acetate [(±)-(8; R = COMe)] is converted into a separable mixture of (–)-isopulegol [(–)-[7; R = H)], (+)-isopulegyl acetate [(+)-(7; R = COMe)], and (±)-neoisopulegyl acetate. Since interconversion with citronellal (9) is easy, this represents a practical resolution of (±)-citronellal.¹⁵ The acetates of menthol and carvomenthol undergo this reaction, but not those of the stable axial alcohols, neomenthyl



⁸ S. L. Dyatkina and B. B. Damaskin, *Elektrokhimiya*, 1974, **10**, 318.

⁹ J. Dillon and K. Nakanishi, *J. Amer. Chem. Soc.*, 1974, **96**, 4056.

¹⁰ G. Balavoine, A. Moradpour, and H. B. Kagan, *J. Amer. Chem. Soc.*, 1974, **96**, 5152.

¹¹ C. T. Flood and D. L. Mills, *J. Amer. Chem. Soc.*, 1973, **95**, 6460.

¹² H. Brunner and H. D. Schindler, *J. Organometallic Chem.*, 1973, **55**, C71.

¹³ J. D. Morrison and W. F. Masler, *J. Org. Chem.*, 1974, **39**, 270.

¹⁴ S. Kumazawa, T. Kato, and Y. Kitahara, *Chem. Letters*, 1973, 633.

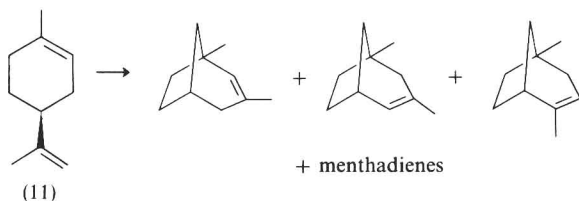
¹⁵ T. Oritani and K. Yamashita, *Agric. and Biol. Chem. (Japan)*, 1973, **37**, 1687.

acetate (5; R = OCOMe) and neocarvomenthyl acetate (10).¹⁶ The further the acetate group is from the asymmetric centre, the lower is the optical yield.¹⁷

New separation techniques for monoterpenoids are liquid chromatography on porous polymer (Hitachi gel 3010)¹⁸ and gas chromatography on graphitized carbon black for the notoriously delicate separation of the menthol isomers (although neo-menthol and menthol are not cleanly separated).¹⁹

2 General Chemistry

Acid-catalysed isomerization of terpenoid hydrocarbons occupies much space in the literature, usually without the emergence of great novelty (see, however, pinenes). The use of mentha-2,8-diene as substrate²⁰ and other hydrocarbons on $\text{TiO}_2\text{--H}_2\text{SO}_4$ catalysts is described.²¹ Liquid-phase rearrangements of pinene and limonene give results varying with acid strength,²² and similar variations occur with basic strength in the base-catalysed rearrangements.²³ By judicious choice of base, it is possible to prepare a particular menthene from one more accessible.²⁴ Rearrangement of limonene (11) in phosphoric acid was known to yield a bicyclic hydrocarbon;²⁵ the latter is shown to be a mixture of three isomers (Scheme 1).²⁶ Isomerization of α -pinene over ferric phosphate



Scheme 1

at 180—560 °C leads to rearrangements and ring-opening to menthanes,²⁷ and heating terpenes with diethyl hydrogen phosphite yields phosphonates, also with rearranged skeletons; pinenes give menthenes, camphene gives isocamphenyl ethylphosphonate, and limonene (11) gives a mixture containing a small amount of a bornyl phosphonate.²⁸

Another paper on the hydration of monoterpenoids in the presence of an ion-exchange resin has appeared (cf. Vol. 4, p. 13).²⁹ Treatment of linalool (12) with chloranil results

¹⁶ T. Oritani and K. Yamashita, *Agric. and Biol. Chem. (Japan)*, 1973, **37**, 1691, 1695.

¹⁷ T. Oritani and K. Yamashita, *Agric. and Biol. Chem. (Japan)*, 1973, **37**, 1923.

¹⁸ M. Nakayama, M. Hiraoka, A. Matsuo, and S. Hayashi, *Nippon Kagaku Kaishi*, 1973, 2314.

¹⁹ V. B. Yakubovich and G. M. Petrov, *Khim. Izmenchivost. Rast.*, 1972, 95.

²⁰ I. I. Bardyshev, Zh. F. Loiko, L. A. Popova, and L. V. Sionskaya, *Doklady Akad. Nauk Beloruss. S.S.R.*, 1973, **17**, 534.

²¹ M. Dul and M. Bukala, *Chem. Stosowana*, 1973, **17**, 19.

²² R. Ohnishi, K. Tanabe, S. Morikawa, and T. Nishizaki, *Bull. Chem. Soc. Japan*, 1974, **47**, 571.

²³ A. Ferro and Y.-R. Naves, *Helv. Chim. Acta*, 1974, **57**, 1152.

²⁴ A. Ferro and Y.-R. Naves, *Helv. Chim. Acta*, 1974, **57**, 1141.

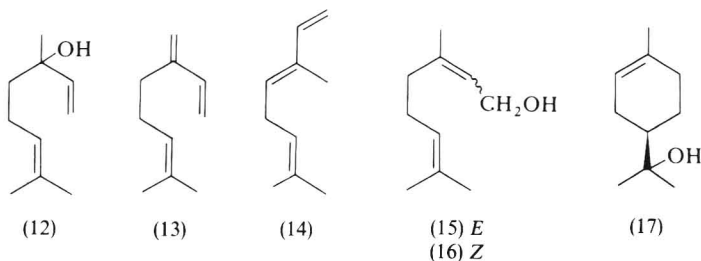
²⁵ V. N. Ipatieff, J. E. Germain, W. W. Thompson, and H. Pines, *J. Org. Chem.*, 1952, **17**, 272.

²⁶ G. Accrombessy, M. Blanchard, F. Petit, and J.-E. Germain, *Bull. Soc. chim. France*, 1974, 705.

²⁷ V. V. Pechkovskii, Yu. P. Klyuev, L. S. Eschchenko, L. N. Shchegrov, V. M. Sycheva, and I. V. Petrashen, *Izvest. Vyssh. Ucheb. Zaved., Les. Zhur.*, 1973, **16**, 107 (*Chem. Abs.*, 1974, **80**, 48 172).

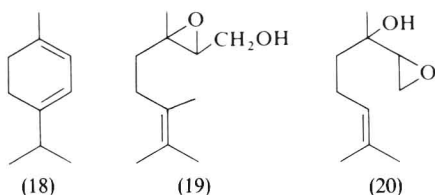
²⁸ R. L. Kennedy and G. S. Fisher, *J. Org. Chem.*, 1974, **39**, 682; Some related work is discussed in the bicyclo[3,1,1]heptane section.

²⁹ Y. Matsubara, T. Fujiwara, and K. Tanaka, *Yuki Gosei Kagaku Kyokai Shi*, 1973, **31**, 924.



in a series of dehydrations and hydrations; myrcene (13), ocimene (14), and their hydration products are formed, but cyclization to menthadienes and subsequent hydration also occur. Geraniol (15), nerol (16), and linalool (12) are interconverted, and give similar products, nerol favouring the cyclized alcohol (17).³⁰ The claim that β -pinene is among the dehydration products of linalool (12) could not be confirmed using boron trifluoride or iodine as catalyst.³¹

Of particular relevance to monoterpenoids is the comparison of reaction parameters for triphenyl phosphite ozonide (TPPO) formation and those of photosensitized oxygenation, where it has been shown that singlet oxygen cannot be a common active species for both types; limonene (11), for example, shows a very different product distribution in the two cases. TPPO oxidation occurs at lower temperatures than ozonide decomposition, and is in some cases, *e.g.* α -terpinene (18), more selective.³² A general study of epoxidation of methylenecyclohexanes, closely related to monoterpenoids, includes a discussion of the epoxide conformations.³³ Epoxidation of allyl alcohols with *t*-butyl hydroperoxide catalysed by vanadium or molybdenum complexes has enabled the new epoxides of geraniol (19) and linalool (20) to be prepared.³⁴ Oxidation of alcohols to ketones (menthol to menthone, borneol to camphor, *etc.*) generally occurs with *N*-chlorosaccharin, but limonene (11) gives a 4-chloro insertion product.³⁵



Details of the highly stereoselective reductions of ketones, (mostly bicyclic monoterpenoids) with alkylboranes are published.³⁶

A new method for alkylating methyl groups *via* π -allyl complexes³⁷ uses geranylacetone as a typical example; this method tackles the general difficulty of making valuable higher terpenoids from cheap monoterpenoids.

³⁰ S. Fujita, Y. Kimura, T. Iguchi, R. Suemitsu, and Y. Fujita, *Nippon Kagaku Kaishi*, 1972, 2140.

³¹ Y. Fujita, S. Fujita, and H. Okura, *Nippon Kagaku Kaishi*, 1974, 132.

³² E. Koch, *Analyt. Chem.*, 1973, **45**, 2120.

³³ A. Sevin and J.-M. Cense, *Bull. Soc. chim. France*, 1974, 963, 969.

³⁴ K. B. Sharpless and R. C. Michaelson, *J. Amer. Chem. Soc.*, 1973, **95**, 6136.

³⁵ J. M. Bachhawat, A. K. Koul, B. Prashad, N. S. Ramegowda, C. K. Narang, and N. K. Mathur, *Indian J. Chem.*, 1973, **11**, 609.

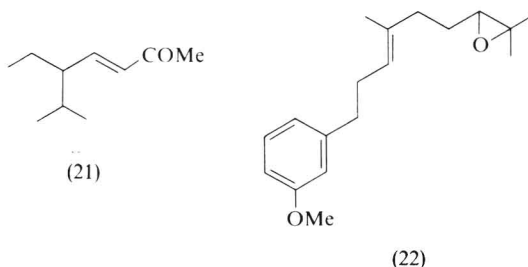
³⁶ H. C. Brown and V. Varma, *J. Org. Chem.*, 1974, **39**, 1631.

³⁷ B. M. Trost, T. J. Dietsche, and T. J. Fullerton, *J. Org. Chem.*, 1974, **39**, 737.

3 Occurrence, Biogenesis, and Biological Activity

A review has appeared on the distribution of terpenoids among different plant species, with sections on biosynthesis and metabolism.³⁸

Some traditional monoterpene plant sources are becoming rarer, adding interest to the flourishing analytical work; examples are the following species: *Artemisia* (several of which contain isothujone),³⁹ *Majorana* and *Origanum* (containing sabinene hydrate),⁴⁰ *Citrus iyo* peel oil (containing several rare oxygenated menthanes),⁴¹ and saffron.⁴² The C₁₀ substance (21) from Greek tobacco is possibly not monoterpene but derived from a diterpene.⁴³ The monoterpene hydrocarbon content of *Cymbopogon* oils varies widely with geographical source (large amounts from Ceylon, small from Java).⁴⁴ A similar study has been made on the monoterpenoids of balsam fir.⁴⁵



A structure-activity correlation study of the substituted monoterpene type (22) of juvenile hormone attempts to show certain structural similarities with ecdysone.⁴⁶ A juvenile hormone antibody has been developed which binds specifically with the naturally occurring hormone, thereby distinguishing it from mimics such as the monoterpenoids.⁴⁷ A large number of variants of the geranyl part of the monoterpene ether juvenoids, including cyclogeranyl, linalool oxide (tetrahydrofuryl), and reduced and oxidized types, have been tested for insecticidal activity.⁴⁸

Pharmacological activities are reported for but-2-ynamine derivatives of borneol and menthol,⁴⁹ and of pinol and camphene.⁵⁰ The full paper on the repellent action of diethylthujamide against the yellow fever mosquito (*Aedes aegypti*) and other insects has appeared (Vol. 3, p. 10).⁵¹

³⁸ H. J. Nicholas, in 'Phytochemistry', ed. L. P. Miller, Van Nostrand, New York, 1973, Vol. 2, p. 254.

³⁹ A. Matsuo, H. Hara, M. Nakayama, and S. Hayashi, *Flavour Ind.*, 1973, **4**, 343.

⁴⁰ G. Marczal and M. V. Vincze, *Gyogyszereszet*, 1973, **17**, 214 (*Chem. Abs.*, 1973, **79**, 149 277).

⁴¹ M. Hiroi and D. Takaoka, *Nippon Kagaku Kaishi*, 1973, 1339.

⁴² A. I. Akhmedov, Sh. K. Chogovadze, M. I. Goryaev, and A. D. Dembitskii, *Maslob-Zhir. Prom.*, 1973, 26 (*Chem. Abs.*, 1973, **79**, 83 384).

⁴³ A. J. Aasen, J. R. Hlubucek, S.-O. Almquist, B. Kimland, and C. R. Enzell, *Acta Chem. Scand.*, 1973, **27**, 2405.

⁴⁴ R. O. B. Wijesekera, A. L. Jayewardene, and B. D. Fonseka, *Phytochemistry*, 1973, **12**, 2597.

⁴⁵ D. T. Lester, *Canad. J. Forest Res.*, 1974, **4**, 55.

⁴⁶ J. F. Grove, R. C. Jennings, A. W. Johnson, and A. F. White, *Chem. and Ind.*, 1974, 346.

⁴⁷ R. C. Lauer, P. H. Solomon, K. Nakanishi, and B. F. Erlanger, *Experientia*, 1974, **30**, 558.

⁴⁸ B. D. Hammock, S. S. Gill, and J. E. Casida, *J. Agric. Food Chem.*, 1974, **22**, 379, 386.

⁴⁹ E. Mariani, M. Longobardi, P. Schenone, F. Bondavalli, and C. Bianchi, *Chim. ther.*, 1973, **8**, 281.

⁵⁰ E. Mariani and P. Schenone, *Educ. Sci.*, 1974, **29**, 113.

⁵¹ V. Hach and E. C. McDonald, *Canad. J. Chem.*, 1973, **51**, 3230.