



A Specialist Periodical Report

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# Terpenoids and Steroids

Volume 3

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between September 1971 and August 1972

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# *General Introduction*

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The aims and presentation follow those of Volumes 1 and 2.

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# *Part I*

## TERPENOIDS



## Introduction\*

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The interesting formal parallel that exists between the rearrangements of the chrysanthemyl cation and the conversion of presqualene alcohol into squalene (and now of prephytoene alcohol into phytoene) has been further explored. Solvolyses<sup>109</sup> of the cyclopropyl (65) and cyclobutyl (63) esters both afford head-to-head coupled C<sub>10</sub> chains analogous to squalene. A versatile new method provides access to 9-substituted *p*-menthanes. This starts with natural limonene and proceeds *via* the anion (135) which retains chirality and leads to chiral products (see below). Skeletal rearrangements in the bicycloheptane series, an historic field in the study of organic reaction mechanisms, has received a fresh impetus from the extended work of Kirmse and his colleagues,<sup>265,266</sup> which is of preparative and mechanistic significance.

Excellence and diversity in the synthetic field again characterize the year's work on sesquiterpenoids, with some notable examples of sophisticated methodology on the industrial scale. The production of C<sub>17</sub> and C<sub>18</sub> juvenile hormones<sup>11,12</sup> and the conversion of the C<sub>17</sub> into the C<sub>18</sub> hormone are cases in point. The metallation of limonene referred to above has been turned to good account<sup>28</sup> in stereospecific routes to bisabolane sesquiterpenoids. The unique antibiotic fumagillin has been synthesized<sup>36</sup> by an imaginative route. Two notable syntheses of zizaene<sup>81,82</sup> have been reported. Wiesner's approach utilized a synthetic route to bicyclo[3.2.1]octanes developed in the course of an approach to diterpene alkaloids. The labile *trans,trans*-1,5-cyclodecadiene system of hedycaryol has been successfully generated by Marshall fragmentation of the appropriate cyclo-octyl tosylate.<sup>108</sup> Ourisson has described<sup>152,153</sup> a simple two-stage procedure whereby the  $\alpha$ -methylene- $\gamma$ -butyrolactone function so widespread among natural sesquiterpenoids can be obtained from the more readily available  $\alpha$ -methyl- $\gamma$ -lactones. The method succeeds only with *cis*-fused lactones. The *in vitro* interconversion of acyclic, mono-, bi-, and tri-cyclic sesquiterpenes and their potential relevance to biosynthesis continue to attract widespread experimental attention<sup>70-76</sup> and the complex acid-catalysed rearrangements of thujopsene have been subjected to penetrating study.<sup>63-66</sup> An attempt<sup>116</sup> to systematize the nomenclature of germacranolides should be noted by workers in the field.

Much effort in the diterpenoid field is concentrated on substances having biological activity. Thus the coleons,<sup>35,36</sup> inumakilactones,<sup>39</sup> and

\* Reference and structure numbers are those of the appropriate chapter.

podolactones<sup>40,41</sup> control the expansion and division of cells. Combined g.l.c. and mass spectrometry has played an important part in the detection and characterization of new gibberellins<sup>99-101</sup> and there have been important advances in gibberellin synthesis.<sup>134,135,140,141</sup> The antheridium-inducing factor of ferns<sup>106</sup> has a gibberellin-like structure. Cyathin A<sub>3</sub>, isolated from the 'bird's nest' fungus, represents a novel mode of cyclization of geranylgeraniol. Notable synthetic successes in the diterpene alkaloid field have come from Wiesner's laboratory in the total synthesis<sup>144</sup> of the delphinine degradation product (158) and the intermediate (159)<sup>145</sup> for a synthesis of songorine.

Cheilanthatriol<sup>1</sup> represents a new type of sesterterpenoid whose carbon skeleton resembles that of triterpenoids.

The structure of Baccharis oxide has been revised;<sup>66</sup> biosynthetically this is close to the previous structure (Vol. 2, p. 168) and therefore of comparable interest. The total laboratory synthesis of lupeol<sup>68</sup> is a notable further achievement in the synthesis of unsymmetrical triterpenoids.

Cornforth and his colleagues have investigated<sup>23</sup> the stereochemistry of isomerization of isopentenyl to dimethylallyl pyrophosphate in isoprenoid biosynthesis. They find that the prototropic change involved is stereochemically different from the superficially analogous association of C<sub>5</sub> units. Bisabolene appears to be excluded as an intermediate in the biosynthesis of helicobasidin and trichothecin by recent labelling studies<sup>59-61</sup> (see also Vol. 1, p. 232, ref. 81) and a 1,4-hydride shift in the initially formed intermediate is indicated. The loss of the C-14 methyl group in cholesterol biosynthesis differs<sup>97</sup> from loss of the C-4 methyl groups. The 32-carbon atom is released at the aldehyde oxidation level as formic acid.

In the carotenoid and polyterpenoid field a number of important stereochemical studies have appeared. These include assignments of the complete stereochemistry of phytoene<sup>11</sup> and lutein<sup>40</sup> and the absolute configurations of abscisic acid<sup>58-60</sup> and the natural irones.<sup>16</sup>

# 1

## Monoterpenoids

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BY A. F. THOMAS

The volume of work published on monoterpenoids is increasing, not only in the absolute sense, but relative to that on other natural products (including other terpenoids). There are at least three possible causes: many monoterpenoids are plentiful, further exploitation is desired, and recent refinements of analytical techniques have made possible the examination of reaction detail that was previously inaccessible. Monoterpenoids lend themselves especially well to such studies because of their suitability for gas chromatography, and also provide examples of a wide variety of structural types. Chemotaxonomy is also increasingly moving toward the use of monoterpenes because of the simplicity of analysis.

Duplication of previously published work (see Vol. 2, p. 5) is reaching new levels. It is incomprehensible that reputable journals (in some cases) with a good refereeing policy still do not detect earlier work—even when it has appeared in this and other reviews—and this year an attempt has been made to quote the earlier reference (this is rarely done by the later authors) in order to highlight the problem.

### 1 Analytical Methods and General Chemistry

The first of two books with monoterpenoid sections is of the 'dictionary' type.<sup>1</sup> It would be useful were it not for the incredible number of errors. Space will not permit a full criticism, but they include incorrect formulae (carquejyl acetate, artemisia and isoartemisia ketones, linalool, linalool oxide, lippione), double bonds of incorrect geometry (yomogi alcohol, cosmene), the inclusion of many discredited or doubtful compounds (santolinenones, osmane, hymenetherene, etc.), and a very unusual biogenetic scheme. The other book purports to give a brief introduction to the chemistry, but terpenoids related to chrysanthemic acid, iridoids, *ortho*-menthanes, and heterocyclic terpenoids are omitted, and there are only 236 references, eight of which are post-1969 and twenty post-1968.<sup>2</sup> Omission of recent literature also spoils a review of photochemistry in the field of monoterpenes:<sup>3</sup> although this has a large literature collection, it is mostly only up to 1969.

<sup>1</sup> T. K. Devon and A. I. Scott, 'Handbook of Naturally Occurring Compounds, Vol. 2, Terpenes', Academic Press, New York, 1971.

<sup>2</sup> D. Whittaker, in 'Chemistry of Terpenes and Terpenoids', ed. A. A. Newman, Academic Press, London, 1972, p. 11.

<sup>3</sup> M. Pfau, *Flavour Ind.*, 1972, **3**, 89. The Specialist Periodical Reports are not quoted among the several reviews listed here.

A method for purifying saturated monoterpenoid hydrocarbons by multistage extractive crystallization with thiourea has been used for menthane, pinane, carane, and 1,1,4-trimethylcycloheptane purification.<sup>4</sup> The results are analogous to distillation or liquid-liquid extraction with greatly increased volatility between components in the two phases in the adduct-formation process. A more specific crystallization process concerns the isolation of 98% pure (–)-menthol by crystallizing the mixture with wintergreen oil or limonene at 5°C.<sup>5</sup> Monoterpenes are also used in a discussion about physical (especially crystallographic) properties of racemates susceptible to spontaneous or induced resolution by crystallization,<sup>6</sup> and a later paper from the same laboratory gives details of the carvoximes and camphoroximes.<sup>7</sup> Gas chromatography of monoterpenoids is included in a paper concerned with an improved calculation of Kováts indices in gas chromatography<sup>8</sup> and the use of various columns is discussed.<sup>9</sup> Retention index data of various substituted cyclohexanes have been used to establish the stereochemistry of various *p*-menthanediols.<sup>10</sup>

A microtechnique for the analysis of monoterpenoids consists of hydrogenolysis in the inlet port of a gas chromatograph and analysis of the saturated hydrocarbons. Certain ring cleavages occur, and *p*-alcohols lose their CH<sub>2</sub>OH group. The products obtained are identified by mass and i.r. spectrometry.<sup>11</sup> The mass spectrometry of some monoterpenoid semicarbazones is reported; many mechanisms are described, but without labelling evidence.<sup>11a</sup>

Terpenoids are frequently used to introduce asymmetry into molecules (a classic example is isopinocampheylborane), and the use of camphor to introduce chirality into lanthanide shift reagents is now established<sup>12</sup> (see also the section on bicyclo[2.2.1]heptanes below). The difference in geminal non-equivalence of methylene hydrogens of diastereomeric (–)-menthoxyacetamides has been used as a monitor for the optical resolution of amines,<sup>13</sup> this being a development of earlier work using menthoxyacetates for diastereomeric alcohols. The optical purity of chiral amines can also be checked from the n.m.r. spectrum of the amides obtained with (+)-(1*R*,4*R*)-camphor-10-sulphonic acid.<sup>14</sup> Use of a menthol ester to separate pseudoasymmetric ferrocenes has been described.<sup>15</sup>

(–)-Menthyl glyoxylate has been used in an attempt to induce asymmetry during a Diels–Alder reaction between the aldehyde group of the glyoxylate and a

<sup>4</sup> F. P. McCandless, *Ind. and Eng. Chem., Product Res. and Development*, 1971, **10**, 406.

<sup>5</sup> Y. Matsubara, H. Hashimoto, J. Katsuhara, and H. Watanabe, *Jap. P.*, 26 933/1971 (*Chem. Abs.*, 1971, **75**, 141 018).

<sup>6</sup> A. Collet, M.-J. Brienne, and J. Jacques, *Bull. Soc. chim. France*, 1972, 127.

<sup>7</sup> J. Jacques and J. Gabard, *Bull. Soc. chim. France*, 1972, 342.

<sup>8</sup> R. U. Luisetti and R. A. Yunes, *J. Chromatog. Sci.*, 1971, **9**, 624.

<sup>9</sup> I. I. Bardyshev and V. I. Kulikov, *Zhur. analit. Khim.*, 1971, **26**, 1857 (*Chem. Abs.*, 1971, **75**, 15 192); T. J. Betts, *Australas. J. Pharm.*, 1971, **52**, S57.

<sup>10</sup> C. Paris and P. Alexandre, *J. Chromatog. Sci.*, 1972, **10**, 402.

<sup>11</sup> R. E. Kepner and H. Maarse, *J. Chromatog.*, 1972, **66**, 229.

<sup>11a</sup> J. Cassan, M. Azarro, and R. I. Reed, *Org. Mass Spectrometry*, 1972, **6**, 1023.

<sup>12</sup> G. M. Whitesides and D. W. Lewis, *J. Amer. Chem. Soc.*, 1971, **93**, 5914; H. L. Goering, J. N. Eikenberry, and G. S. Koerner, *ibid.*, p. 5913.

<sup>13</sup> T. G. Cochrane and A. C. Huitric, *J. Org. Chem.*, 1971, **36**, 3046.

<sup>14</sup> G.-A. Hoyer, D. Rosenberg, C. Rufer, and A. Seeger, *Tetrahedron Letters*, 1972, 985.

<sup>15</sup> S. I. Goldberg and W. D. Bailey, *Tetrahedron Letters*, 1971, 4087.

1-alkoxybutadiene. In the simple case the optical yield was very low,<sup>16</sup> but it rose to 25% when the reaction was effected in the presence of Lewis acids at low temperatures.<sup>17</sup> Another attempt at inducing asymmetry in a Diels-Alder reaction used (–)-dimenthyl fumarate and isoprene. The optical yield rose from 0% at atmospheric pressure to 4.7% at 5000 atmospheres.<sup>18</sup>

The preferred rotational conformations of acetyl and formyl groups can be predicted by temperature-dependent c.d. measurements, and the technique has been applied to some monoterpene aldehydes.<sup>19</sup> The sign of the Cotton effect has been related to the chirality of a series of  $\pi$ -molecular complexes of monoterpene (and other) hydrocarbons with tetracyanoethylene. Inconclusive results found with (+)-sabinene were ascribed to complexation with the cyclopropane ring.<sup>20</sup>

## 2 Biogenesis, Occurrence, and Biological Activity

An excellent review, particularly where it concerns his own work, has been published by Banthorpe<sup>21</sup> which covers the whole field of monoterpene biogenesis. The same author has examined the biosynthesis of (+)-pulegone in *Mentha pulegium*, in which [2-<sup>14</sup>C]mevalonic acid gave unequal labelling, almost all the tracer being associated with the isopentenyl pyrophosphate part of the molecule, in agreement with earlier work (Vol. 2, p. 6). 3,3-Dimethyl[1-<sup>14</sup>C]acrylic acid, on the other hand, appeared to be incorporated after degradation to acetate units.<sup>22</sup> The conversion of monoterpenes into carotenoids in *Tanacetum vulgare* and *Artemisia annua* has been found to occur in whole plants either as undegraded C<sub>10</sub> units or as 3,3-dimethylallyl pyrophosphate equivalents.<sup>23</sup> Some studies on *in vitro* tissue cultures of *T. vulgare* were also made.<sup>24</sup>

In this plant the petals contain  $\beta$ -D-glucosides of isothujol, neoisothujol, and other compounds, and it is observed that [2-<sup>14</sup>C]mevalonate incorporation into the glucose portion is ten times more than into the terpenoid portion.<sup>25</sup> Results not in agreement with Banthorpe's unequal labelling have been obtained by Suga *et al.*, who fed [2-<sup>14</sup>C]mevalonic acid to twigs of *Cinnamomum camphora* Sieb. var. *linalooliferum* and found the linalool to be equally labelled.<sup>26</sup> When [2-<sup>14</sup>C]mevalonate is fed through cut stems of *Mentha piperita* in the presence of sucrose, the incorporation into the monoterpenes is markedly increased. This was interpreted as support for the compartmentation of sites of monoterpene

<sup>16</sup> J. Jurczak and A. Zamojski, *Tetrahedron*, 1972, **28**, 1505.

<sup>17</sup> O. Achamatowicz, jun. and B. Szechner, *J. Org. Chem.*, 1972, **37**, 964.

<sup>18</sup> B. S. El'yanov, E. I. Klabunovskii, M. G. Gronikberg, G. M. Parfenova, and L. F. Godunova, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1971, 1658.

<sup>19</sup> T. Suga, K. Imamura, and T. Shishibori, *Bull. Chem. Soc. Japan*, 1972, **45**, 545.

<sup>20</sup> A. I. Scott and A. D. Wrixton, *Tetrahedron*, 1972, **28**, 933.

<sup>21</sup> D. V. Banthorpe, B. V. Charlwood, and M. J. O. Francis, *Chem. Rev.*, 1972, **72**, 101. The carquejol formula is incorrect in this review (see Vol. 1, p. 35 of these Reports).

<sup>22</sup> D. V. Banthorpe, B. V. Charlwood, and M. R. Young, *J.C.S. Perkin I*, 1972, 1532.

<sup>23</sup> D. V. Banthorpe, H. J. Doonan, and A. Wirz-Justice, *J.C.S. Perkin I*, 1972, 1764.

<sup>24</sup> D. V. Banthorpe and A. Wirz-Justice, *J.C.S. Perkin I*, 1972, 1769.

<sup>25</sup> D. V. Banthorpe and J. Mann, *Phytochemistry*, 1972, **11**, 2589.

<sup>26</sup> T. Suga, T. Shishibori, and M. Bukeo, *Phytochemistry*, 1971, **10**, 2725.