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ON THE BORDERLINE BETWEEN BIOLOGY AND TECHNOLOGY

Reaction wood is a favorite research field for wood technologists. The aim of such studies consists in finding a causal explanation for the extraordinary accomplishment of which this tissue is capable when heavy trunks deviated from their natural position are geotropically bent by growth in an attempt to regain their original orientation with respect to the gravitational field.

Two observations are taken into consideration: 1st) that so called compression wood expands when freed from adjacent normal wood (1) and 2nd) that the expansion equals numerically the shrinkage of this wood during drying. This led to the hypothesis "that the stresses developed by compression wood are related to imbibition of water by the fibre walls and the resulting anisotropic swelling"(2).

Such reasoning neglects the fact that the formation of reaction wood occurs under optimum hydration conditions. Therefore, the technological concept of a swelling mechanism cannot explain the cause of the stresses observed. It is true that, since osmotic forces are too weak (3), only chemical forces (including hydration) are capable of producing the stresses necessary for bending an old conifer trunk. However, these stresses are not developed by a post festum hydration of produced reaction wood, but while its cell walls are growing!

According to our New Zealand colleagues (4,5,6), it is not the fibrillar cellulose which is hydrated, but the hemicelluloses of the matrix in the secondary cell wall. Therefore, this matrix in compression wood must develop a stronger affinity to water, or the arrangement of its fibrils must display a flatter helix than in normal tracheids. Considering the figures published by HEIJNOWICZ (2), the second possibility must be ruled out. So the cell wall of compression wood ought to contain a more highly hygroscopic matrix than those of tracheids previously laid down. As a consequence, the stress involved must be active from the very beginning in the growing wall of the cells derived from the cambium.

Whether the task of producing a longitudinal stress by growth can be fulfilled only by hydration phenomena is questionable. Since growth involves synthesis of cell wall substances, stresses can just as well be produced by the intercalation of compounds which expand in situ by chemical processes (e.g. polymerisation, incrustation etc.). This embodies the old concept of intussusception which must be declared as an essential growth process because it could be shown how the matrix increases its volume by incorporation of Golgi vesicles into the expanding cell wall (7). These findings indicate that the spectacular manifestation of "active reaction wood" can hardly be explained in technological terms based in simple features of water imbibition, because growth, i.e. one of the most complicated biological phenomena, is involved.

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MONOTERPENOIDS OF CONIFERALES

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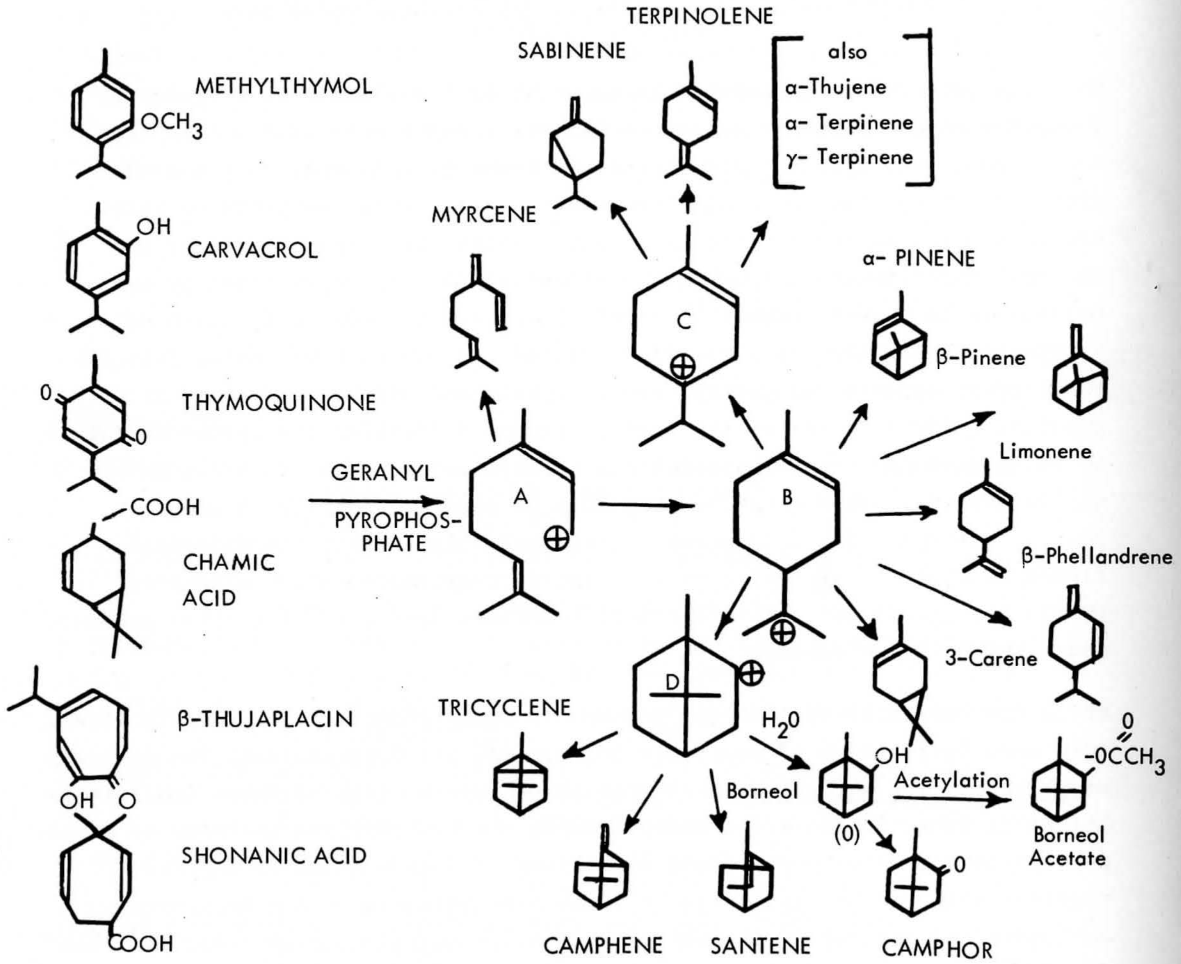
The botanical order Coniferales is composed of three families - Pinaceae, Taxodiaceae and Cupressaceae and includes a large number of the most important forest tree species. The tissues of trees of this order often produce aromatic, honey-like materials termed oleoresins, volatile parts of which are designated as turpentines or essential oils. The largest part of the chemical constituents composing the essential oils is represented by monoterpenoids in a great number of cases. These are the compounds which arise biosynthetically through a reaction sequence involving mevalonate, 3-isopentenyl pyrophosphate and geranyl pyrophosphate and can be recognized in a great majority of cases by the possibility of dissecting the carbon skeletons of their formulae into two isopentane -"Isoprene" - units. In addition to monoterpenoids, other constituents, such as sesquiterpenoids (3 isoprene units), diterpenoids (4 isoprene units), and occasionally the materials formed by other biosynthetic paths, such as n-hydrocarbons, n-aldehydes (fatty acid path) and methyl chavicol (shikimic acid path) are often present, sometimes in large amounts.

While the essential oils of the members of Taxodiaceae are only poorly known, much more information is available on Pinaceae and Cupressaceae. The majority of <u>aliphatic and alicyclic</u> monoterpenoids common to both of these families is listed in Table 1. The differences between the two families in terms of these constituents involve more common occurrence in Cupressaceae of sabinene together with the biosynthetically close terpinolene, α-and γ-terpinenes, α-thujene and related oxygenated materials. In addition, d-limonene is often found in Cupressaceae while in Pinaceae l-limonene is invariably present. Most of these terpenoid hydrocarbons were found to exert growth retardant influence on some wood damaging fungi (1).

Larger differences are apparent in <u>aromatic</u> monoterpenoids. While in Pinaceae this class is represented only by methyl thymol (<u>Abies balsamea</u>) and neither thymol nor methyl thymol have been so far identified in Cupressaceae, other aromatic monoterpenoids are quite common in Cupressaceae and include carvacrol, hydrothymoquinone, their methyl ethers and products of oxidative coupling as well as thymoquinone. Another class of aromatic monoterpenoids, that of tropolones is also quite common in this family, occasionally accounting for the majority of the volatile oil from wood. Both terpenoid phenolics and tropolones were found to be very toxic to some wood destroying fungi (2).

TABLE I

FORMULAS AND BIOSYNTHETIC RELATIONSIPS OF SOME MONOTERPENOIDS FROM CONIFERALES



Further materials characteristic of Cupressaceae are the monoterpenoid acids of a number of structural types (e.g. chamic and shonanic acids).

Among the monoterpenoid compounds normal hydrocarbons seem to be characteristic for Pinaceae, or more precisely for the genus Pinus of this family where they occur in wood of certain species, occasionally almost completely substituting for the monoterpenoids.

The composition of the essential oils is not constant but is subject to variations, often very strong, within a plant (from resin producing tissue to resin producing tissue and also within tissues), between plants (genetic) as well as in response to the environmental conditions.

The influence of the environment seems to be the smallest. Although relatively little work has been done in this area, the evidence obtained so far indicates that the corresponding variability can be assumed to be within experimental error of analysis for practical purposes. Thus, Hanover (16), investigated the composition of the essential oil from the cortical oleoresin of clonally propagated populations of Pinus monticola, grwoing under three distinctly different sets of soil, moisture and other climatic and site conditions in Idaho and found only negligible differences.

The between-tissue differences seem to be much more serious. As the first approximation and excluding roots the oleoresin producing tissues of Coniferales can be considered to be of five types:

1. Oleoresin system of xylem
2. Oleoresin system of foliage
3. Oleoresin system of phloem
4. Oleoresin system of cortex
5. Oleoresin system (or systems) of fruit

Accordingly materials from each of these tissues should be investigated separately. In many cases, particularly with phenolic and tropolonic constituents, separate consideration of materials obtained from heart- and sapwood is also necessary.

The resin system of wood of many species (Pinus, Picea, Pseudotsuga and Larix) involves the presence of extracellular resin ducts from which oleoresin exhudes upon wounding. Other species lack these ducts; essential oils in these cases can be obtained by extraction using neutral organic solvents and/or by steam distillation of wood.

Bark (all tissues from cambium towards outside) represents a complex material, poorly investigated as far as its resin systems are concerned. Cortex is smooth, grey to whitish primary bark tissue, which in most cases is sloughed off at a relatively young age. Occasionally, as in some Abies species it remains on the stem until relatively old age - often over 100 years; commonly, it is covered with blisters which contain cortical oleoresin, occasionally erroneously called balsam ("Canada balsam").

The difference in the composition of the essential oils from the wood and leaf tissues can probably best be exemplified by Pinus jeffreyi and Pinus sabiniana. The essential oil from wood of either of these species is composed essentially of n-heptane with minor amounts of other normal hydrocarbons such as n-nonane and n-undecane. Monoterpenoids are present only in traces. On the other hand, the essential oils of leaves of these species are composed mainly of α- and β-pinenes with smaller amounts of other monoterpenoids; n-heptane and related materials are absent (3).

The difference between the essential oil of foliage and cones can also be large. Thus leaves of *Cupressus sargentii* and *Cupressus macrocarpa* contain α-pinene to 5.5 and 9.7% only; in cones of the same species on the other hand the amount of α-pinene rises to 86.2 and 90.5% respectively (3).

The composition of phloem and cortical essential oils of the bark from several *Abies lasiocarpa* trees are given in Table II. As can be seen, the differences encountered are much larger than experimental error and strongly suggest that in any phytochemical work the two tissues should be separately considered.

Table II

Cortical and Phloem Essential Oil from Four *Abies lasiocarpa* Trees

		α-pinene	β-pinene	3-carene	myrcene	limonene	β-phellandrene
Tree 1	cortex	18.0	21.5	-	.5	35.5	23.5
	phloem	41.0	33.5	-	.5	3.5	21.5
Tree 2	cortex	14.5	11.5	-	1.5	42.0	28.5
	phloem	39.5	15.5	-	3.5	11.0	29.0
Tree 3	cortex	9.5	1.0	17.0	3.0	63.5	3.0
	phloem	28.5	2.0	43.0	9.0	16.0	1.5
Tree 4	cortex	21.5	12.0	11.5	1.5	23.0	29.0
	phloem	43.5	14.5	13.0	1.0	8.5	18.5

The differences within tissues can be also of sizeable magnitude and can be separated into two categories:

1. Variability in time
2. Variability in space

The influence of day-time, season and age on the composition of the essential oils has been examined by several investigators and found to be rather small as long as mature plant portions were used. With young, developing tissues, on the other hand, the systematic changes encountered were considerable. Thus JUVONEN (4) reported that α-pinene content of *Pinus sylvestris* current year needles rose from 7.4 to 36.4% from June to the end of August, with other monoterpenoids undergoing in most cases similar changes. Comparable results were found by KEPNER (5) on *Pseudotsuga menziessii* needles (increase in citronellol and related materials with aging) and by ZAVARIN, COBB and BERGOT (6) on the *Pinus ponderosa* needles (increase in methyl chavicol with aging).

The influence of time on the yield of oleoresin or essential oil has been found to be somewhat more serious. Thus wood was reported to yield more oleoresin in summer than in winter (7), the per cent of essential oil in wood oleoresin of *Pseudotsuga menziessii* (8) has been found to increase from 32.5% in June to 40.2% in October, and the yield of essential oil from needles of several species has been found to be the highest between January and April and between September and November (9).

The influence of the relative within plant location where a sample was obtained has been reported as negligible with wood, although in all cases only mature portions of the tree trunk have been sampled. In the case of cortex, the results indicate larger variability towards the top of the trees. Thus ZAVARIN (10) found that systematic changes of the essential oil composition were about 18 times as large in the younger parts (latter 30% of the total age) of the II *Abies* trees belonging to four species; e.g. in one *Abies magnifica* tree, the content of β-pinene limonene and camphene changed from 35, 3 and 20% to 24, 16 and 34% respectively, within the last 20 year portion remaining relatively constant within the older - 20-80 year - tree portion.

With needles higher yields of essential oil are generally obtained using younger material. Influence of the position of the branch has also been noted; thus JUVONEN and LAKO (II) reported gradual drop of the oil yield from top (0.82%) to bottom (0.21%) of one *Picea abies* tree.

Thus, although it seems that in many cases the variability within resin-producing tissues is not large, occasionally it can become significant. Ascertaining the magnitude of this variability before proceeding with the experimental work as well as keeping away from the areas of high metabolism (unless they form the subject of a particular investigation, of course) seems to be a good rule.

Genetic variability of the essential oil composition is probably the largest in magnitude and can be of importance on all taxonomic levels.

Table III

Turpentine Composition of *Pinus torreyana* Gum Oleoresin
Population: Del Mar, California*

Sample No.	n-Heptane	n-Nonane	α-Pinene	n-Undecane	β-pinene	Myrcene	Limonene	β-Phellandrena	Cineole	Peak 0.65	n-Decyl aldehyde	Longifolene	Total terpenes
239	2.0	0.5	2.5	6,0	0,5	2,0	85.5	-	2,0	0.5	tr	3.5	24.0
240	2.5	1.5	3.0	6.5	tr	2.5	84.0	tr	1.0	0.5	0.5	3.5	24.5
241	2.5	1.5	2.5	5.0	tr	4.0	84.0	0.5	0.5	1.0	1.0	4.0	26.5
242	3.0	2.0	2.5	6.0	0.5	3.5	82.0	0.5	0.5	0.5	0.5	4.5	25.0
243	1.0	1.5	2.5	7.0	tr	2.0	86.0	tr	1.0	0.5	0.5	4.0	24.0
244	2.5	1.5	2.5	6.0	tr	3.0	85.5	-	2.5	0.5	0.5	3.5	25.5
245	2.0	1.5	3.0	6.0	tr	4.0	83.0	0.5	tr	tr	tr	2.0	26.0
246	2.5	1.5	3.0	7.0	tr	4.0	82.0	tr	1.0	0.5	0.5	4.0	24.5
247	2.0	1.5	2.5	6.0	0.5	2.0	85.5	-	2.0	0.5	tr	3.0	24.0
248	2.5	2.0	2.5	6.0	0.5	3.0	83.5	-	tr	0.5	0.5	5.0	26.0
249	2.5	1.9	3.0	5.5	tr	2.5	85.0	-	0.5	0.5	0.5	2.0	25.0
250	2.5	2.0	3.0	6.0	tr	2.5	84.0	tr	0.5	0.5	0.5	4.5	24.5
251	1.5	2.0	3.0	6.0	0.5	2.5	84.5	-	0.5	0.5	0.5	5.5	21.5
Mean	2.2	1.7	2.7	6.1	0.2	2.9	84.2	0.1	0.9	0.5	0.4	3.8	24.7
Mean dev.	0.4	0.2	0.2	0.4	0.25	0.6	1.1	0.15	0.5	0.1	0.2	0.8	0.9

* in per cent of total terpenes. Last column per cent of total oloeresin.

The variability on the individual level is exemplified by the Tables III and IV. As can be seen, the variability of the Del Mar population of Pinus torreyana is very low, approaching the experimental error. This can be understood from the small size of this population (few thousand trees) and its long isolation, permitting intensive inbreeding. On the other hand the variability of the cortical essential oil of Abies lasiocarpa is extremely high, with limonene fluctuating from 0.5% to 88% and with corresponding changes in the case of many other terpenoids. This variability is not paralleled by any morphological differences and is thus purely chemical in character. It stresses the necessity to use statistically sound procedures in any phytochemical work and not to rely on the analysis of a single individual. It should be pointed out that high variability on the individual level is more common with cases like that of Pinus torreyana being less frequently encountered.

Table IV

Turpentine Composition of Abies lasiocarpa Cortical Oleoresin
Population: Bighorn Nat.Forest, Wyoming
Terpene basis

Herb.Sample No.	-pinene	Camphene	-pinene	3-Carene	Myrcene	Limonene	-phellandrene	Terpinolene	Total terpenes
788	13.0	tr	24.0	0.5	tr	1.5	60.5	0.5	39.8
789	9.0	tr	0.5	1.0	1.5	88.0	tr	tr	28.3
790	14.0	0.5	1.5	13.0	1.0	68.0	1.5	0.5	27.2
791	6.0	tr	14.5	14.0	1.0	30.0	33.5	1.0	32.5
792	6.5	0.5	0.5	4.5	-	87.5	tr	0.5	28.7
793	4.5	tr	0.5	17.0	1.0	75.0	1.0	1.0	28.2
794	9.5	tr	15.5	12.5	1.0	23.0	37.5	1.0	27.6
795	7.5	0.5	2.5	20.5	1.0	66.5	0.5	1.0	27.8
796	8.5	0.5	7.5	14.5	3.0	55.5	10.0	0.5	34.3
797	10.5	0.5	8.5	27.0	2.0	31.0	19.0	1.5	25.7

Table V

Turpentine Composition of Abies lasiocarpa Cortical Oleoresin
Population: Togwotee Pass, Wyoming
Terpene basis

410	13.5	tr	2.0	6.0	1.0	77.0	0.5	-	
411	2.0	tr	0.5	10.0	tr	86.5	1.0	-	
412	2.5	tr	2.0	6.5	0.5	88.0	0.5	tr	
413	6.5	0.5	5.0	11.5	0.5	75.0	0.5	0.5	
414	5.0	tr	4.5	12.0	0.5	77.0	0.5	0.5	

Table VI

Turpentine Composition of Abies lasiocarpa Cortical Oleoresin
Population: Crater Lake, Oregon
Terpene basis

584	8.0		22.5	15.0	0.5	2.0	51.0	1.0	25.2
585	13.5		26.0	10.0	1.0	1.5	48.0	-	28.4
586	8.0		25.5	2.0	tr	2.5	62.5	-	22.9
260	7.0		25.0	6.0	0.5	2.5	58.5	0.5	23.0
261	3.5		25.5	10.0	0.5	2.0	58.5	tr	27.6
282	7.5		24.5	5.5	0.5	1.5	60.5	tr	32.0
284	9.0		23.5	8.0	0.5	2.5	55.5	1.0	27.6
285	7.5		25.0	9.0	1.0	1.5	55.5	0.5	27.7

The cases of chemical variabilities on the population level (geographic variabilities) without concurrent morphological variabilities also seem to be common. Tables V and VI exemplify the analyses of the cortical essential oils of Abies lasiocarpa from the Pacific coast (Crater Lake, Oregon) and from the Rocky Mountains (Togwotee Pass, Wyoming). While in coastal populations, limonene is found in negligible amounts, in the Rocky Mountain material it is the main constituent, with β-pinene and β-phellandrene decreasing to near zero (12).

In most cases, however, the morphological differences parallel the chemical differences making the latter useful as taxonomic markers. For instance, Abies concolor from California and Oregon is known to be morphologically different from that of the Rocky Mountains. The two are considered even as two different species by many European botanists while in the United States they are not commonly given even varietal status. Investigation of the cortical essential oil of these two taxa pointed out the sharp chemical difference existing between the two. The Rocky Mountain material contained sizeable amounts of both camphene and 3-carene, which are lacking for all practical purposes in the California and Oregon populations (12).

Another example is the case of Pinus muricata - Bishop pine. This pine grows in several locations on the California and Baja California coast only a few miles inland, as well as on the islands near-by. The coastal populations have been separated by DUFFIELD (13) on the basis of morphology into 1.) the northern variety "borealis" (with bluish foliage, incompletely serotinous cones, and dense, narrow crowns), extending from near Annapolis towards the north (38^{o} 41.5'-41^{o} 3.5'latitude) 2.) southern variety "muricata" including populations from San Luis Obispo, Lompos and Baja California (with greenish foliage, completely serotinous cones and spreading crowns), (35^{o}10.5' to 31^{o}15'latitude), with the 3.) remaining populations between Annapolis and down south to and including Monterey, given the intermediate status (38°41.5' to 36°33.5' latitude).

In 1964 the crucial chemotaxonomic study of FORDE and BLIGHT (14) appeared, followed two years later by investigations of MIROV et al., (15). It has been found that all populations north of Annapolis (variety "*borealls*") contained wood turpentines composed essentially of α-pinene; the turpentines of the southern variety "*muricata*" were largely composed of a mixture of sabinene and terpinolene while those of intermediate populations contained mainly 3-carene. The geographic separation of the three chemical races was surprisingly sharp. Although the α-pinene and 3-carene races were found to come together and naturally hybridize near Annapolis, the hybridization area was very small, only a few hundred yards in length. A single putative hybrid between the 3-carene and sabinene races has also been found near Lompoc. These chemical investigations pointed out that the differences within *P.muricata* might be more significant than thought before. This has been substantiated by CRITCHFIELD finding a very strong hybridization barrier between the sabinene and 3-carene races.

Biosynthesis of monoterpenoids. As a by-product of the studies of genetic variability mentioned before, quantitative correlations between amounts in which individual constituents are occurring are often obtained. These can be helpful occasionally for elucidation of some aspects of their biogenesis in the following way. As mentioned before, geranyl pyrophosphate represents the intermediate through which the synthesis of monoterpenoids is generally assumed to take place. The best way to visualize this is to postulate the existence of the carbonium ion A formed from geranyl pyrophosphate (Table 1). The actual occurrence of this carbonium ion has never been proven and it most likely represents only the biological equivalent; i.e., a distorted reflexion of biosynthetical reality useful only in so far as it allows easier comprehension of processes (probably concerted) involved. This carbonium ion can transform itself into other carbonium ions (B, C and D) through a series of simple reactions involving intramolecular attack of the double bond by the positively charged atom and hydride shifts. Each of these carbonium ions represents a rather energy rich entity and can stabilize itself through loss of a proton under formation of a new bond or through hydration to an alcohol. The hydrocarbons and/or alcohols formed can then react further, by enzymatic oxidation of the alcohol to a ketone, acetylation of the alcoholic group to acetate ester, reduction of the double bonds, etc. (Table I). The number of basic carbonium ions from which the monoterpenoids of Coniferales form are

essentially four and accordingly the monoterpenoids can be biosynthetically grouped into four families, (fenchene and related monoterpenoids, being very rare, are excepted).

One of the effects of this mode of formation is that biosynthetically close compounds, belonging to the same biosynthetic family, i.e., synthesized through the same carbonium ion, are likely to occur together in a given source. This, of course, does not hold strictly as the enzyme specificity can, and occasionally does, create a situation where distantly related terpenoids are found together under exclusion of all others. Still, these situations are rarer and the likelihood is there when sabinene is found in a certain source, for terpinolene, α-thujene, α- and γ-terpinenes to be also present in detectable amounts. Similarly, when camphene is found in another source, it is a good idea to look for tricyclene, santene, borneol, camphor or bornyl acetate. Conversely, co-occurrence of two or more compounds in a number of sources can be used as an argument for their biogenetic closeness. The arguments of this nature are not restricted, of course, to the terpenoid field but are quite commonly applied in other areas of natural products. They are rather speculative, but very useful.

Somewhat more reliable promises to be the mentioned before quantitative corollary of this co-occurrence. In several cases a quantitative relationship has been found between amounts of several constituents of essential oils. For instance the relationship between camphene, tricyclene and bornyl acetate in cortical oleoresin of a number of fir species was found to be always 1.0 : 0.09 : 1.45, on the basis of several hundreds of samples run and without a single exception (12), with the corresponding correlation coefficients better than 0.95. At the same the total % of these three monoterpenoids fluctuated drastically. This is, of course, nothing else but the reflexion of the mode of biosynthesis depicted above. It indicates the lack of enzymatic control over the stabilization of 2-bornane carbonium ion (D) to the three compounds in question, and represents another argument supporting the above biosynthetic scheme.

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