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HYDROGENOLYSIS OF TERPENES IN THE INJECTION PORT OF A GAS CHROMATOGRAPH

II. SESQUITERPENES*

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SUMMARY

Hydrogenation and hydrogenolysis in the injection port of a gas chromatograph (carbon skeleton technique) was applied to sesquiterpenes. Acyclic, mono-, bi- and tricyclic sesquiterpenes were chosen. The reaction products of the acyclic mono-terpenes could be easily identified. Both nerolidyl acetate and *trans*-β-farnesene gave farnesane. Hydrogenation of the monocyclic sesquiterpene α-curcumene gave the expected dihydrocurcumene while elemane was formed from β- and γ-elemene. The ten-membered monocyclic sesquiterpenes, germacrene B and D and germacrone gave a large number of reaction products, which were mostly bicyclic. The formation of germacranes was dependent on the hydrogenation temperature. The bicyclic ses-quiterpenes β- and δ-selinene gave two main reaction products. Others, however, belonging to the classes of the cadinanes, muurolanes and amorphanes, formed more compounds than was expected. The tricyclic sesquiterpenes thujopsene, α-cedrene and longifolene gave two products each, which is in accordance with the results obtained by hydrogenation over platinum dioxide in solution. From the results it became clear that the technique is a valuable tool in the identification of sesquiterpenes when only small amounts are available.

INTRODUCTION

For the identification of small amounts of sesquiterpenes when no reference compounds and spectra are available, the application of the technique of carbon skeleton analysis yields information of great importance. Such a technique, based on hydrogenation and hydrogenolysis, was developed by Beroza and co-workers[1] and was recently applied to monoterpenes[2-4]. No extensive studies on sesquiterpenes using Beroza's technique have yet been published. Some examples were mentioned by Galfré and Guiochon[4] and only a small number of mass spectra[5-7] and Kováts indices[8,9] of hydrogenated sesquiterpenes are available.

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An investigation was therefore made of the hydrogenation and hydrogenolysis of a number of mono-, bi- and tricyclic sesquiterpenes using a neutral palladium catalyst in the injection port of a gas chromatograph.

EXPERIMENTAL

Materials

The compounds used were obtained either through the generosity of other workers in the field or by isolation from the appropriate essential oils or by synthesis from other sesquiterpenes (Table I). Purities were determined by gas–liquid chromatography (GLC) and identities by infrared and mass spectrometry.

Catalyst

A neutral type of palladium catalyst (2% as the metal) on acid-washed Chromosorb W, 60–80 mesh, was prepared as follows. A 330-mg sample of palladium chloride was dissolved in 100 ml of 50% aqueous acetic acid by heating on a hot-plate

TABLE I

SOURCES OF SESQUITERPENES

Compound	Isolated from	Supplied by
α-Amorphene	Muhuhu oil	—
δ-Cadinene	Elemol sample	
α-Curcumene	*Curcuma amara* oil	
Germacrene-D	*Mentha aquatica* oil	
Caryophyllene	—	Dr. F. Rijkens,
Longifolene		Naarden International B.V.,
Valencene		Naarden, The Netherlands
β-Sinensal	—	Dr. P. Schudel,
		Givaudan-Esrolko A.G.,
		Zürich, Switzerland
Cedrol	—	Dr. R. E. Erickson,
Thujopsene		Givaudan Corporation.
		New Jersey, U.S.A.
Germacrone	—	Dr. T. H. E. Tattje,
		University of Groningen,
		The Netherlands
α-Muurolene	—	Dr. E. von Sydow,
γ-Muurolene		Swedish Institute for
ε-Muurolene		Food Preservation Research,
		Göteborg, Sweden
α-Cedrene	—	Synthesized*
β-Elemene		
γ-Elemene		
trans-β-Farnesene		
Germacrene-B		
Nerolidyl acetate		

* These compounds were synthesized from other sesquiterpenes by Dr. R. J. C. Kleipool of the Organic Synthesis Department of this Institute.

for about 1 h with occasional swirling by hand. The solution was cooled, 200 mg of anhydrous sodium carbonate were added and the solution was evaporated to dryness in contact with 10 g of Chromosorb W in a rotary film evaporator. The catalyst preparation was then heated in an oven at 110° for 1 h.

For hydrogenolysis reactions, approximately 0.5 g of the catalyst was packed into an injection port tube (12 × 0.5 cm) to give a catalyst column 10 cm in length. The catalyst was activated in the injection port with a hydrogen flow-rate of 25 ml/min for 0.5 h at 150° and for 1–3 h at 280°.

Gas chromatography equipment

A Hewlett-Packard Model 5750 gas chromatograph equipped with dual flame ionization detectors and a Carle thermistor detector was used. The chromatographic columns used were a 10 ft. × 1/8 in. O.D. stainless-steel tube packed with 5% Apiezon L on 60–80 mesh Chromosorb W-AW, and two 500-ft. × 0.03 in. I.D. stainless-steel capillary columns, one coated with Carbowax 20M and the other with SF-96 (50). The exterior ends of the injection ports were fitted with water-cooled jackets so as to keep the septums cooled at the high temperatures of the hydrogenolysis experiments.

Hydrogenolysis experiments

The 10-ft. Apiezon L column, attached to the exit end of the injection port tube packed with catalyst and equipped with the thermistor detector, was used in the hydrogenolysis studies. The injection port temperature was 150–180° in hydrogenation and 280° in hydrogenolysis experiments. The column temperature was 150° and the detector temperature 180°. The carrier gas was hydrogen at the flow-rate of 25 ml/min in all experiments. The compounds being studied were dissolved in *n*-heptane and the heptane solutions (10–20%, v/v) injected directly on to the head of the catalyst column.

Reaction products were trapped either as a mixture or as individual components, using 12-in. glass capillaries cooled in liquid nitrogen.

Some compounds were also hydrogenated in acetic acid or ethyl acetate over Adams catalyst when enough material was available.

Determination of Kováts indices

The so-called self-consistent Kováts indices[8] were measured relative to caryophyllene, humulene and cuparene. A solution of the reaction products in heptane and a heptane solution of the reference sesquiterpenes were injected together on to the Carbowax 20M and SF-96 (50) columns. The column temperatures were isothermal at 130° on the Carbowax 20M column and 150° on the SF-96 (50) column.

Spectral analysis

The mass spectra of the reaction products were determined using a gas chromatograph–mass spectrometer–computer combination. The SF-96 (50) capillary column was connected to a Varian Mat CH 4 mass spectrometer by way of a membrane separator.

Infrared spectra were run on a Perkin-Elmer Model 257 spectrophotometer with a sample dissolved in carbon tetrachloride in an ultra-micro-cavity cell. Purification of the reaction products for IR analysis was carried out on 4 m × 4 mm I.D.

TABLE II

HYDROGENATION AND HYDROGENOLYSIS OF SESQUITERPENES

Compound	Reaction products "Identity"	Temperature (°C)	%	Kováts index SF-96 (50)	Kováts index Carbowax 20M	Spectra	Ref.
Acyclic							
Nerolidyl acetate	Farnesane	190	100	1392	1362	IR, MS	7, 13
trans-β-Farnesene	Farnesane	200	100	1392	1360	IR, MS	7, 13
β-Sinensal	3,7-Dimethyldodecane	160	95	1327	1340	MS	
Monocyclic							
α-Curcumene	Dihydrocurcumene	220	75	1448	1696	IR, MS	13
	Bisabolane-a		17	1448	1492	MS	7
	Bisabolane-b		8	1458	1510	MS	7
β-Elemene	Elemane	200	80	1404	1460	IR, MS	7, 13
γ-Elemene	Elemane	200	80	1403	1460	IR, MS	7, 13
Germacrene-B	Elemane	160	4	1403	1457	IR, MS	7, 13
	Germacrane-b		20	1477	1572	MS	
	Germacrane-c		49	1482	1585	MS	
	Germacrane-d		25	1489	1593	MS	
	4αH,5αH-Eudesmane		2	1497	1636	MS	7
Germacrene-D	Cadinane-a (?)	160	4	1437		MS	6
	Eudesmane isomer		13	1456		MS	
	Eudesmane isomer		19	1460		MS	
	Germacrane-b		13	1475		MS	
	Germacrane-c		22	1479		MS	
	Unknown		9	1487		MS	
	Germacrane-d		9	1489		MS	
	4αH,5αH-Eudesmane		10	1495		MS	7
Germacrone	Hexahydrogermacrone-a	150	58	1585*	1950*	MS	
	Hexahydrogermacrone-b		25	1590*	1938*	MS	
	Hexahydrogermacrone-c		17	1600*	1967*	MS	
Hexahydroger-macron (mixture of isomers)	Unknown (M+ = 204)	270	3	1400		MS	
	Germacrane isomer?		4	1419		MS	
	Germacrane isomer?		1	1432		MS	
	Cadinane-a?		21	1443		MS	6
	Cadinane-b?		4	1456		MS	6
	Eudesmane isomer		18	1460		MS	
	Eudesmane isomer		16	1463		MS	
	Germacrane-b		9	1476		MS	
	Germacrane-c		15	1480		MS	
	Germacrane-d		4	1487		MS	
	4αH,5αH-Eudesmane		2	1495		MS	7
Bicyclic							
β-Selinene	4βH,5αH-Eudesmane	200		1405	1582	IR, MS	14
	4αH,5αH-Eudesmane			1497	1635	IR, MS	7, 15
	Eudesmane isomer			1459		MS	
	Eudesmane isomer			1462		MS	

TABLE II *(continued)*

Compound	Reaction products						
	"Identity"	Reaction conditions		Type of evidence			
		Temper- ature (°C)	%	Kováts index		Spectra	Ref.
				SF-96 (50)	Carbo- wax 20M		
δ-Selinene	4βH,5αH-Eudesmane	200		1404	1578	IR, MS	14
	4αH,5αH-Eudesmane			1497	1632	IR, MS	7, 15
	Eudesmane isomer			1458		MS	
	Eudesmane isomer			1461		MS	
Valencene	Valençane (nootkatane)	180	95	1493	1624	MS	5
Caryophyllene	Caryophyllane-a	180	40	1425	1522	IR, MS	5,7,13
	Caryophyllane-b		33	1432	1533	IR, MS	5,7,13
	Caryophyllane-c		8	1450	1555	IR, MS	5,7,13
	Caryophyllane-d		19	1450	1562	IR, MS	5,7,13
Tricyclic α-Cedrene	?	160	2	1449	1600		
	8βH-Cedrane		23	1458	1617	MS,NMR	16
	8αH-Cedrane		75	1465	1627	MS,NMR	16
Cedrol	α-Cedrene	180	27.5	1431		MS	
	8βH-Cedrane		16.5	1455	1617	MS	
	8αH-Cedrane		56.0	1463	1625	MS	
Thujopsene	Tetrahydrothujopsene-a	160	80	1496	1668	MS	
	Tetrahydrothujopsene-b		20	1508	1678	MS	
Longifolene	?	190	14	1424	1575		
	7αH-Longifolane		37	1460	1627	MS,NMR	17
	7βH-Longifolane		49	1467	1633	MS,NMR	17

* Column temperature, 170°. Kováts index relative to *n*-hydrocarbon.

aluminium columns packed with 20% Lac-1R-296 or Apiezon L on Chromosorb W-AW-DMCS, 60–80 mesh. When the amount of sample was sufficient, NMR spectra were measured at 60 MHz on a Jeol 60 H instrument.

RESULTS AND DISCUSSION

The number of different sesquiterpene skeletons found in nature is still increasing[10-12]. About 30 main skeletons are known, representing more than 70% of the sesquiterpenes, and the remaining 30% can be described by about 70 less common skeletons[12].

For this study, sesquiterpenes belonging to several classes with different skeletons were hydrogenolyzed. The choice of these compounds was influenced by both structural importance and availability.

The results are summarized in Tables II and III and Figs. 1–11. For some compounds, the steric configurations could be ascertained by comparing IR and NMR spectra with published spectra. This was impossible with most of the bicyclic sesquiterpenes; only the muurolanic, cadinanic or amorphanic nature of the reaction products could be determined by comparing mass and IR spectra and Kováts indices with literature data.

TABLE III

REACTION PRODUCTS OF α-AMORPHENE (XXI), α-, γ-, ε-MUUROLENE (XXII, XXIII, XXIV) AND δ-CADINENE (XXV)

Component No.	Kováts index, SF-96 (50)	"Identity"	Evidence*	Reaction products (%)				
				XXI	XXII	XXIII	XXIV	XXV
XXVI- 1	1438	Cadinane-a	MS, KI	9.8	25.7	13.9	17.2	19.7
- 2	1445	Muurolane-a	MS, KI	3.0	7.2	16.7	11.7	2.1
- 3	1450	Muurolane-c	MS	—	7.4	11.3	11.5	2.4
- 4	1452			—	2.8	1.0	2.5	2.2
- 5	1455	Amorphane-a (isocadinane)	MS, KI	11.5	—	—	—	—
- 6	1457	Cadinane-b	MS, KI	—	18.7	18.2	21.6	32.2
- 7	1459	Eudesmane-isomer	MS, KI	12.0	—	—	—	—
- 8	1460	Muurolane-d	MS	—	2.8	8.0	10.4	6.0
- 9	1461	Eudesmane-isomer	MS, KI	5.0	—	—	—	—
-10	1466			3.5	5.8	3.5	6.0	—
-11	1471	Cadinane-c	MS, KI	3.5	11.7	8.4	8.6	21.2
-12	1487	Amorphane-b	MS, KI	6.5	—	—	—	—
-13	1496	Muurolane-b	MS, IR, KI	4.0	11.8	16.8	9.4	4.2
-14	1498	4αH,5αH-Eudesmane?	MS, KI	9.5	—	—	—	—
-15	1522	Calamenene	MS, KI	31.5	5.8	2.9	1.3	10.2
-16	1583	See Fig. 7	MS	—**	—**	—**	—**	—**

* KI = Kováts index.
** Present in the reaction mixture but not measured quantitatively.

The Kováts indices from the literature were corrected relative to caryophyllene. Those on Carbowax 20M were even then sometimes ten or more units lower than those found by Andersen and co-workers[8,9].

A large number of reaction products was formed from the germacrenes, germacrone and some bicyclic sesquiterpenes. It was not always possible to correlate a peak in a chromatogram on the SF-96 (50) column with one in the chromatogram
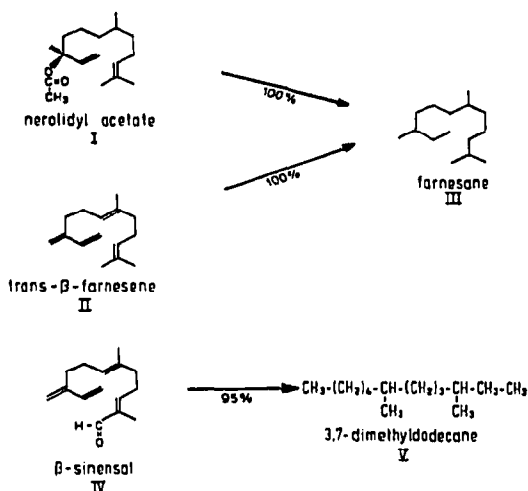

Fig. 1. Hydrogenolysis of acyclic terpenes.

of the same mixture on the Carbowax column. In these cases, only the Kováts index on the SF-96 (50) column is given.

Acyclic sesquiterpenes

In Fig. 1 and Table II the results of the hydrogenolysis of three acyclic sesquiterpenes are presented. Nerolidyl acetate (I) and trans-β-farnesene (II) were converted quantitatively into farnesane (III). β-Sinensal (IV) gave as the main product (V), the hydrocarbon resulting from the loss of the $-C{\overset{\displaystyle O}{\underset{\displaystyle H}{}}}$ group.

Monocyclic sesquiterpenes

In Figs. 2, 3 and 4 and in Table II the results of the hydrogenolysis of a number of monocyclic sesquiterpenes are presented. a-Curcumene (VI) gave three reaction products; dihydrocurcumene (VI-1) was the main product and two bisabolanes (VI-2 and VI-3) were formed as minor products (Fig. 2). The Kováts index of the bisabolanes agreed fairly well with those of bisabolane I and II found by Andersen and Falcone[8]. The mass spectra of these two compounds showed only minor differences and agreed well with that published by Moshonas and Lund[7] for bisabolane.

Hydrogenation of β- and γ-elemene (VII and VIII) resulted in elemane (IX) as the main compound (Fig. 2) and three minor components (M$^+$ = 210) with mass spectra which differed only in relative intensities from that of elemane (IX).

Germacrene-B (X) and germacrene-D (XI) gave a large number of reaction products. At high reaction temperatures (>180°), only bicyclic compounds (M$^+$ = 208) were formed. At 150°, germacranes were also among the reaction products (Fig. 3). The mass spectra of the germacranes did not show a molecular mass (M$^+$ = 210) peak; the highest visible mass number was 167. From germacrene-B a trace amount of elemane was formed.

Germacrene-D (XI) also gave three germacranes with the same Kováts indices on the SF-96 (50) column as those of germacrene-B.

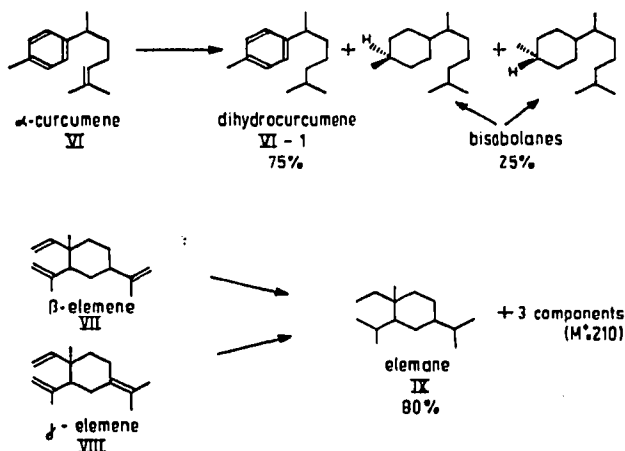Besides the germacranes, a number of hydrogenated bicyclic sesquiterpenes

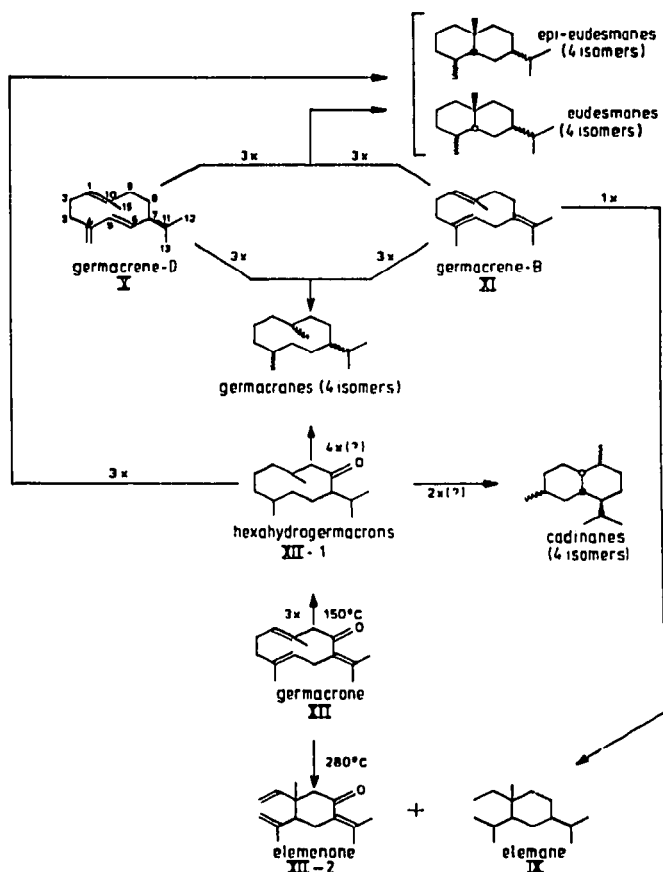Fig. 2. Hydrogenation of α-curcumene, β-elemene and γ-elemene.

Fig. 3. Hydrogenolysis and hydrogenation products formed from germacrene-B and germacrene-D and from germacrone. The figures on the arrows indicate the number of isomers actually formed and the figures in parentheses indicate the number of possible isomers.

was formed (Fig. 3). One of these is probably selinane, which was also obtained by Endo *et al.*[18] from a germacrene alcohol by reduction in acetic acid over Adams catalyst.

From the mass spectra, it was concluded that the other bicyclic products (M^+ = 208) were not muurolanes (*m/e* 164 < *m/e* 166), amorphane-b (*m/e* 124 < *m/e* 123) or cadinanes (*m/e* 193), but were probably eudesmanes.

Germacrone (XII) was hydrogenolyzed in two steps (Fig. 3); at low temperature (150°), hexahydrocompounds (XII-1) (three isomers) were formed and this mixture was further reduced at 280°. Hydrogenolysis in one step at 280° was also carried out, which gave hexahydroelemenone (XII-2) and elemane[19]. The two-step reaction, in addition to bicyclic products and the same three germacranes as above, resulted in two other monocyclic components (highest visible mass number *m/e* 167). Only four stereoisomeric germacranes are possible. These two other monocyclic components are not elemanes (no visible M^+ = 210); their mass spectra are somewhat different from those of the three germacranes and in particular *m/e* 69 is much lower in intensity.

It is uncertain whether or not one of these components is the fourth germacrane.

The mass spectra and the Kováts indices of the bicyclic products indicate that the same three eudesmanes (including selinane) are formed which were found in the reaction mixture from the hydrogenation of germacrene-B and -D.

Two components are formed that are not muurolanes, eudesmanes or amorphane-b, but probably cadinanes.

Fig. 4 shows the chromatogram on the SF-96 (50) column and the so-called mass chromatograms of mass 165, 167, 193 and 208 of the reaction products of hexahydrogermacrone.

Bicyclic sesquiterpenes

Eudesmane (selinane) type. The results of the hydrogenation of β- and δ-selinene (XIII and XIV) are presented in Table II and Fig. 5. From both compounds, four reaction products were formed with the same mass spectra and Kováts indices.

According to its IR spectrum[15], mass spectrum[7,15] and Kováts index[8], one component is 4αH,5αH-eudesmane (XV) or selinane. The other main component was identified as 4βH,5αH-eudesmane (XVI); its IR spectrum agreed well with a published spectrum[14] of this compound.

Contrary to the results of other investigators[8,13,14], compound XVI rather than XV is the main product with this type of catalytic hydrogenation of β-selinene.

The steric configuration of the other two compounds cannot be given because of lack of information in the literature. Assuming that an *exo–endo* shift[20] takes place and that the double bond in the isopropylidene group migrates toward the ring[21,22], β-selinene can give six reaction products. These components can also be formed, in addition to two other ones, from δ-selinene by 1,4-addition followed by reduction of the double bond.

Eremophilane type. The results of the reduction of valencene are given in Table II and Fig. 6. The main product formed was valençane (nootkatane) according to its mass spectrum[5] and the Kováts indices[8].

Caryophyllane type. Although only one IR spectrum[22] and one mass spectrum[5,7] could be found in the literature, four reaction products are to be expected from caryophyllene (XIX) and were indeed obtained (Table II and Fig. 6). The highest visible mass number in all spectra is 152, which, with mass number 124, is characteristic[5] of caryophyllanes (XX). The spectral evidence is, however, insufficient to assign structures to the four compounds obtained.

Cadinane type. This type of starting product yielded the most complex group of reaction products investigated (Fig. 7, Table III). A large number of sesquiterpenes (amorphanes, muurolanes, bulgaranes and cadinanes) belong to this group. From all of the compounds (no bulgaranes were available) that were hydrogenated, a large number of reaction products was obtained, but no steric configurations were determined. The spectra and Kováts indices were compared with literature data[5,6,8,9,13]. The mass spectra of the muurolanes and of amorphane-b were characteristically different from those of the cadinanes:

      muurolanes: m/e 164 > m/e 166, base peak m/e 109;
      amorphane-b: m/e 124 > m/e 123, base peak m/e 109;
      cadinanes: base peak m/e 109.

The compounds α-amorphene (XXI), α-, γ- and ε-muurolene (XXII, XXIII, XXIV)

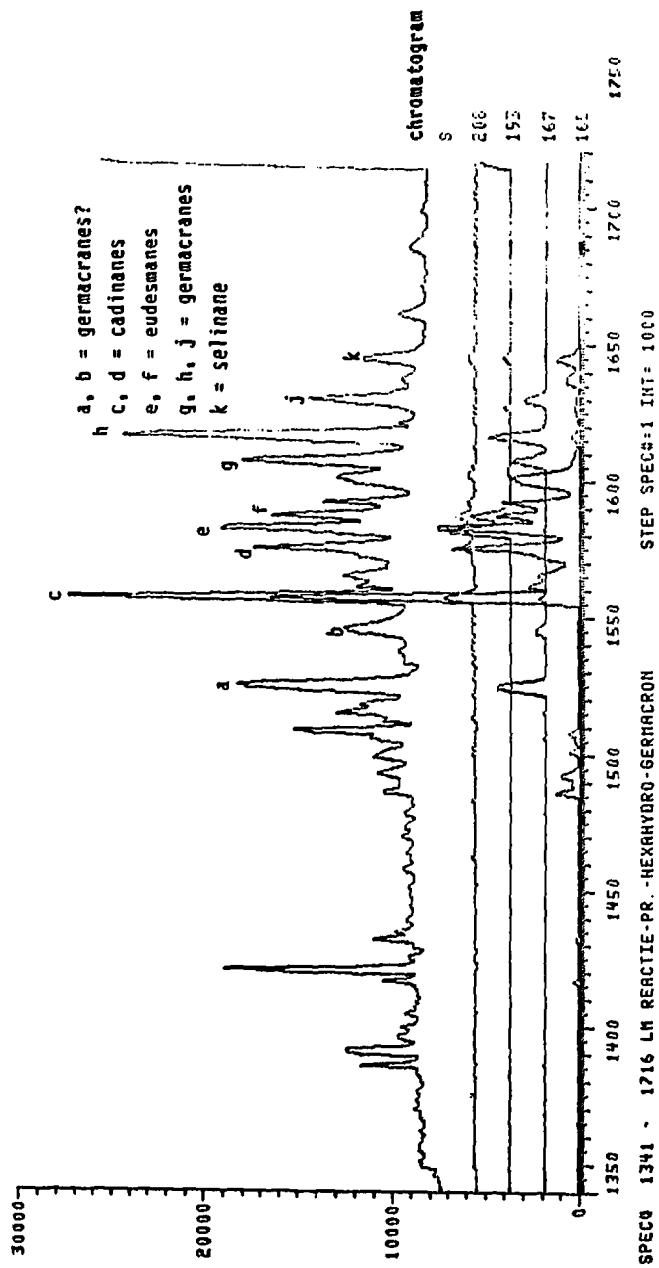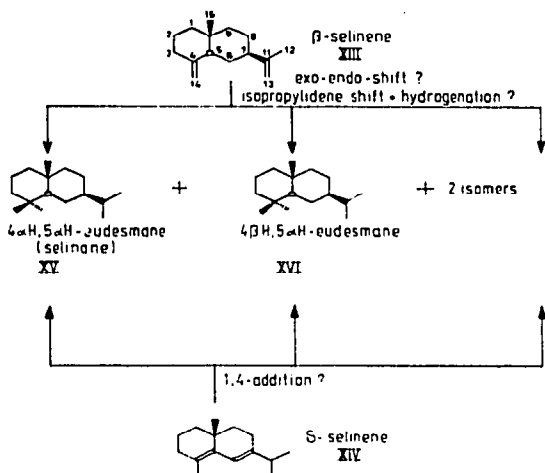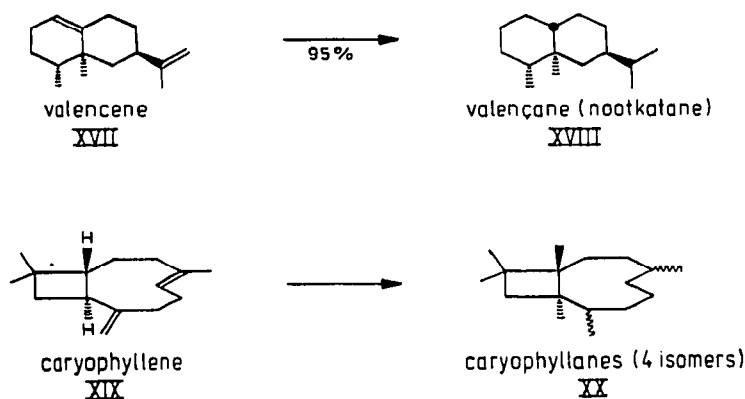Fig. 4. Chromatogram and mass chromatograms of the hydrogenation products of hexahydrogermacrone.

Fig. 5. Hydrogenation of β- and δ-selinene.

CIVO-TNO G 3672

Fig. 6. Hydrogenation of valencene and caryophyllene.

and δ-cadinene (XXV) gave very similar reaction products (Table III) at a reaction temperature of 150–180°.

Five products formed from α-amorphene were not found as reaction products from the other compounds. One of these (XXVI-5) is amorphane-a[6] (also named isocadinane[23] and amorphane I[9]) and another (XXVI-12) is amorphane-b (also named tetrahydroamorphene, peak 2[23] or amorphane II[9]). The other three components (XXVI-7, -9 and -14) all show an $m/e = 193$ ($M^+ - 15$) in their mass spectra. This mass fragment is not observed in the spectra of the muurolanes, amorphanes or cadinanes but is a characteristic fragment of those saturated bicyclic sesquiterpenes which have an angular methyl group. The Kováts index on SF-96 (50) and the mass spectra of these three components are the same as those of selinane (XV) and the two other minor reaction products of β- and δ-selinene (Fig. 5). Insufficient α-amorphene
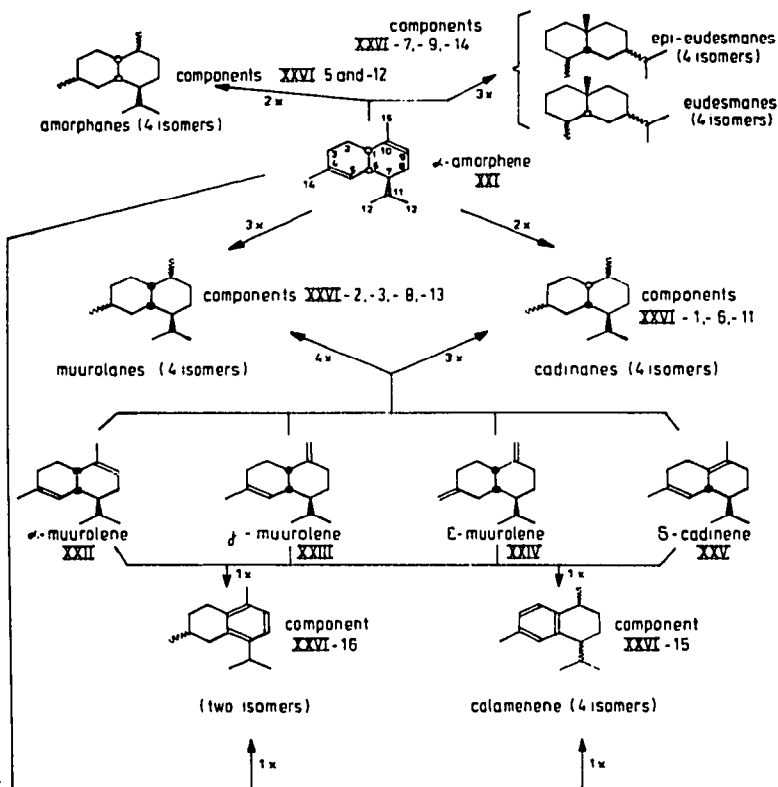
Fig. 7. Hydrogenation of cadinane-type sesquiterpenes. The figures on the arrows indicate the number of isomers actually formed and the figures in parentheses indicate the number of possible isomers.

was available to isolate component XXVI-14 from the reaction mixture and definitely to identify it as selinane from its IR spectrum.

From the muurolenes and from δ-cadinene four products and from α-morphene three products were formed, with m/e 164 $>$ m/e 166 (Table III). According to the IR and mass spectra[5,6], component XXVI-2 is muurolane-a and component XXVI-13 is muurolane-b. The other two products (XXVI-3 and -8) are probably the other two muurolane isomers.

Components XXVI-1, -6 and -11 are the main reaction products from the muurolenes and from δ-cadinene; components XXVI-1 and -11 are also formed from α-amorphene. These three components have the same Kováts indices on both capillary columns as cadinane I, II and III, respectively, obtained by Andersen and co-workers[8,9] by reduction of γ-cadinene in acetic acid over Adams catalyst.

The aromatic reaction products (XXVI-15 and -16) were obtained from all products.

Although the steric configuration of the reaction products could not be elucidated, it is clear that in all instances more reaction products are formed than are to be expected when no changes in the position of the bridge hydrogen atoms take place. The formation of selinanes from α-amorphene is conceivable only when the ring
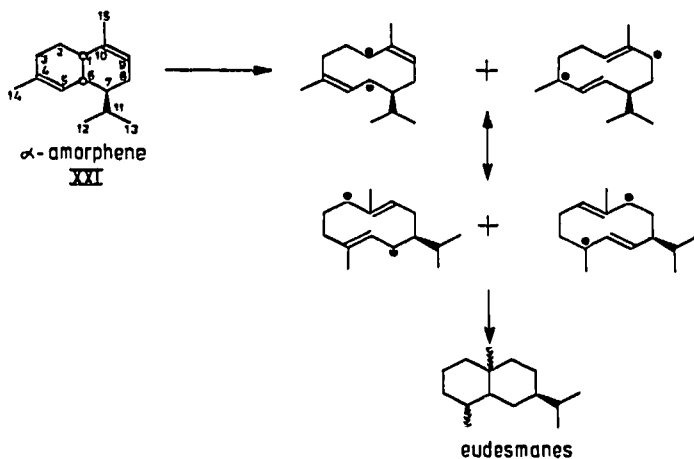
Fig. 8. Proposed formation of eudesmanes from α-amorphene. Pd on Chromosorb-W, 150°.

opens between C_1 and C_6; it is known that selinane is formed from germacrenes[18]. Bi-radicals could be formed as intermediates from α-amorphene at the high reaction temperatures (Fig. 8).

If component XXVI-7, -9 and -14 are indeed eudesmanes, no explanation can be given for the fact that these components are not formed from the muurolenes and δ-cadinene.

Tricyclic sesquiterpenes

Cedrane type. α-Cedrene and cedrol were hydrogenolyzed and the results are given in Table II and Fig. 9. Three reaction products were obtained from α-cedrene, of which the two most abundant were 8αH- and 8βH-cedrane (XXVIII, XXIX). Some contradiction exists about the nomenclature of these compounds. They are named cedrane and isocedrane by Galfré and Guiochon[4] and in *Chemical Abstracts*, but iso-cedrane and cedrane by Acharya and Brown[16].

In order to find out which of the two products was 8αH-cedrane, α-cedrene was reduced in acetic acid over Adams catalyst. According to the NMR spectrum of
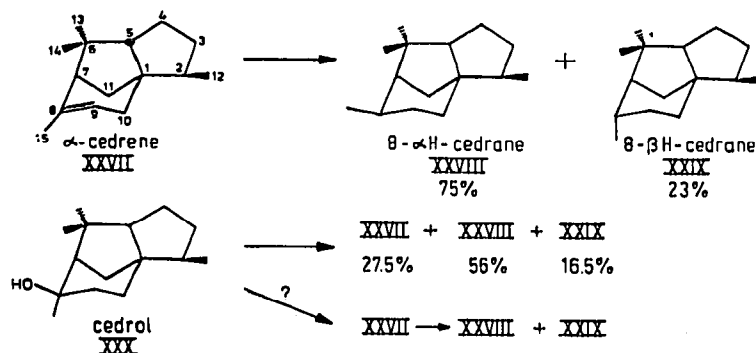

Fig. 9. Hydrogenation and hydrogenolysis of α-cedrene and cedrol.

the two-component reaction mixture, the main component (95%) was 8αH-cedrane[16,24]; the other is, therefore, the 8βH-isomer. These two components had the same Kováts indices and mass spectra as the two main products obtained by GLC hydrogenation of α-cedrene; 8βH-cedrane leaves both columns just ahead of the 8αH-isomer.

Cedrol gave four reaction products and unreacted cedrol when it was hydrogenolyzed at 180°. The two main reaction products were 8αH- and 8βH-cedrane. It is of interest that α-cedrene was also formed. Galfré and Guiochon[4] suggest that hydrogenolysis of an alcohol on palladium–Chromosorb is a two-step reaction: dihydration catalyzed by Chromosorb, followed by hydrogenation of the hydrocarbon catalyzed by palladium. Indications of the correctness of this assumption are that α-cedrene is one of the reaction products and the ratio of 8αH- to 8βH-cedrane is 3.3:1, as it is when α-cedrene is reduced (Table II).

Thujopsane type. The results of the hydrogenation of thujopsene (XXX) are presented in Table II and Fig. 10. Two tetrahydro products are formed.

It is known that by catalytic hydrogenation (palladium/carbon or platinum dioxide) in ethanol, a dihydro compound is initially formed by 1,4-addition of hydrogen. This product is then further hydrogenated to give two tetrahydro compounds[25]. In order to ascertain whether or not the end-products are the same in both cases, the dihydro and tetrahydro compounds were synthesized by hydrogenation of thujopsene in ethanol over palladium/carbon. The dihydro compound was identified as XXXII by comparing its NMR spectrum with that given by Norin[26].

By comparing the IR spectra and the Kováts indices on both columns, it was shown that the tetrahydro compounds XXXIII and XXXIV were indeed the same compounds as those formed by hydrogenation in the GLC injection port. The hydrogenation products of thujopsene formed over palladium on Chromosorb in the GLC
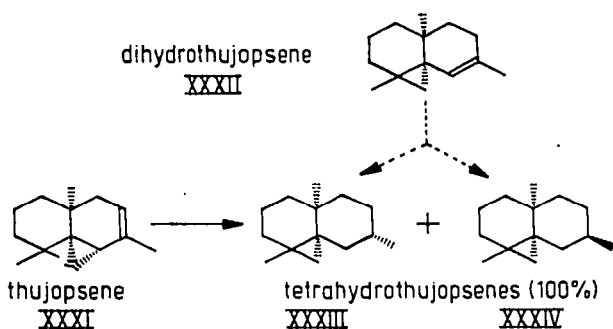

Fig. 10. Hydrogenation of thujopsene.

injection port are undoubtedly the result of a 1,4-addition of hydrogen to the α,β-unsaturated cyclopropane system with opening of an external cyclopropane ring bond and further reduction of the dihydro compound.

Longifolane type. Longifolene (XXXV) was hydrogenated; the results are given in Table II and Fig. 11. Two reaction products, 7αH- and 7βH-longifolane (XXXVI

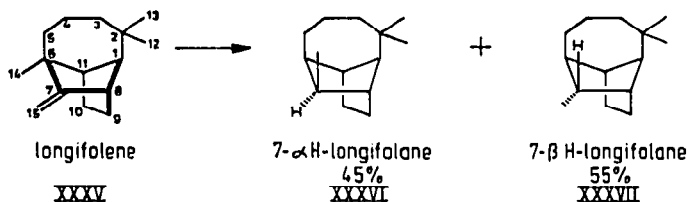Fig. 11. Hydrogenation of longifolene.

and XXXVII) were obtained. In order to find out which of the two compounds was 7αH-longifolane, the hydrogenation was also carried out in ethyl acetate and acetic acid over Adams catalyst. According to Carnduff and Ourisson[17] the ratio of the two isomers is dependent on the solvent used. The results calculated from the NMR spectra of the reaction mixtures are given in Table IV. From these data, assignments in the chromatograms can be based on the peak ratios. The ratio of the α- and β-isomer obtained by hydrogenation over palladium on Chromosorb in the GLC injection port could now be calculated from the chromatogram of the reaction mixture (Table IV).

TABLE IV

HYDROGENATION OF LONGIFOLENE

Method of hydrogenation	7αH-longifolane (XXXIV)		7βH-longifolane (XXXV)	
	This study (%)	Carnduff and Ourisson[17] (%)	This study (%)	Carnduff and Ourisson[17] (%)
Adams catalyst–ethyl acetate	55	54	45	46
Adams catalyst–acetic acid	34	44	66	56
Pd–Chromosorb	45		55	

CONCLUSION

The use of the carbon skeleton technique is undoubtedly a valuable tool for the identification of sesquiterpenes. It is, however, useful only if reference data on mass spectra and Kováts indices are available. This study was undertaken and will be continued in order to compile these data, among other objectives, including a comparison of the results of the catalytic reduction in solution and in the vapour phase.

From this study, it can be concluded that care has to be taken in judging the results of catalytic reduction in the vapour phase. In general, it can be said that during vapour phase hydrogenation other products can be formed than those obtained in solution at room temperature. In order to reduce the chance of "artifact" formation, it is advisable to hydrogenate first at low temperature (150°) before hydrogenolysis at high temperature (250°). In particular, the germacrane-type sesquiterpenes are easily converted into another type of sesquiterpene.

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