REACTION GAS CHROMATOGRAPHY

II. DEHYDROGENATION OF MONOTERPENE COMPOUNDS ON PLATINUM–ALUMINA CATALYST[*]

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A previous communication from this laboratory reported that catalytic dehydrogenation of cyclohexane derivatives can be accomplished through "reaction gas chromatography" on a micro-scale with considerable saving of time[1]. The technique appeared to be of special promise in the study of terpenoids which constitute one of the largest groups of pharmaceutically important natural products possessing six-membered alicyclic rings. Dehydrogenation gas chromatography of a few monoterpene compounds was reported by OKAMOTO AND ONAKA[2]. Employing a reactor packed with palladium on silica gel, the authors found that the seven monoterpenes, which they investigated, could be classified into two groups: one consisting of monocyclic compounds possessing a *p*-menthane skeleton and bicyclic compounds cleaving easily to yield this skeleton, and the other consisting of bicyclic and alicyclic monoterpenes not readily dehydrogenated to *p*-cymene. Their study, based on experiments with only seven compounds, lacked data on product yields and did not give a comprehensive correlation between structural features of monoterpenoids and ease of aromatization. The present authors carried out a detailed investigation on forty-two monoterpene compounds including hydrocarbons, alcohols, esters, aldehydes and ketones. It is the purpose of this paper to report the results obtained and discuss the mechanisms of some of the dehydrogenations and isomerizations which were observed.

EXPERIMENTAL

Apparatus

       Gas chromatographs. Three gas chromatographs were used in this study:

       (1) The Burrell Kromo-Tog K-2 equipped with a thermal conductivity detector and used in conjunction with the reactor. Column: 20 % Reoplex 400 prepared as previously described[3].

       (2) The Aerograph Autoprep 700 equipped with a thermal conductivity detector. Column: Aluminum tube (length 12 ft., O.D. 3/8 in.) packed with silicone nitrile XE-60 (10 %) deposited from chloroform solution on acid-washed Chromosorb W.

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(3) The Aerograph Hy-FI 600-C, equipped with a hydrogen flame ionization detector. Column: Stainless steel tube (length 5 ft., O.D. 1/8 in.) packed with silicone rubber SE-30 (3%) deposited from chloroform solution on acid-washed silanized Chromosorb W.

The latter two gas chromatographs were employed for comparing retention times of dehydrogenation products with those of pure reference samples.

Reactor. It was assembled as previously described[1].

Catalyst. 5 % Platinum on alumina prepared as previously described[1].

Procedure

Dehydrogenation. Dehydrogenation was effected by injecting the sample into the reactor at the required temperature. Sample size depended on the nature of the substance examined and the column temperature.

Identification of reaction products. Products obtained were identified by comparison of retention times (Reoplex 400, silicone nitrile XE-60 and silicone rubber SE-30 columns) with those of pure reference samples. Effluents from the Reoplex 400 column were collected in carbon disulphide and samples collected were rechromatographed on XE-60 and SE-30 columns. Their identity was confirmed by infrared spectrophotometry.

RESULTS AND DISCUSSION

Hydrocarbons

Most of the terpene hydrocarbons were aromatized to *p*-cymene. Table I shows the results obtained when the reactor was operated at 220°. The tendency of mono-

TABLE I

YIELD OF *p*-CYMENE BY DEHYDROGENATION GAS CHROMATOGRAPHY OF TERPENE HYDROCARBONS
Reactor temperature: 220°. Column temperature: 110°. Helium: 75 ml/min.

No.	Hydrocarbon	Classification	p-Cymene (%)
1	α-Terpinene	Monocyclic	97
2	α-Phellandrene	Monocyclic	95
3	Limonene	Monocyclic	95
4	Terpinolene	Monocyclic	95
5	3,8-*p*-Menthadiene	Monocyclic	95
6	3-Menthene*	Monocyclic	36
7	*p*-Menthane	Monocyclic	20
8	Sabinene	Bicyclic	90**
9	3-Carene	Bicyclic	90
10	α-Pinene	Bicyclic	80
11	β-Pinene	Bicyclic	80
12	Camphene	Bicyclic	< 5
13	Myrcene	Acyclic	75
14	Ocimene	Acyclic	10***
15	*allo*-Ocimene	Acyclic	10***

* Isomerised partially to carvomenthene (26 %).
** Mixture of 90 % *p*-cymene and 10 % terpinolene, as determined by rechromatography on SE-30 column.
*** Per cent based on unpolymerised fraction.

cyclic terpenes to aromatize may be correlated to the number of double bonds present in the molecule. Thus *p*-menthadienes were almost quantitatively converted into *p*-cymene, while 3-menthene and *p*-methane yielded only 36 % and 20 % of *p*-cymene, respectively. The extent to which bicyclic terpenes aromatized depended on the nature of the rings in the molecule. Sabinene and 3-carene behaved like menthadienes. The cyclopropane ring in these molecules split readily and yields of *p*-cymene were high. α-Pinene and β-pinene, possessing cyclobutane rings were also effectively aromatized to *p*-cymene. The five-membered ring of camphene proved to be comparatively resistant to aromatization. The behaviour of acyclic monoterpenes appeared to be governed by the geometry of the double bonds. Conjugate diene groups of these compounds acquired preferentially *s-trans* configurations[4]. Thus, myrcene gave a high yield of *p*-cymene while ocimene and *allo*-ocimene showed little tendency to cyclize and aromatize (Fig. 1). Ocimene gave *allo*-ocimene and some lower boiling compounds, also obtained from the latter isomer. Both compounds underwent significant polymerizations.

Dehydrogenation became less effective as the temperature was reduced. At lower temperatures isomerisation was the predominant reaction. Most of the terpenes
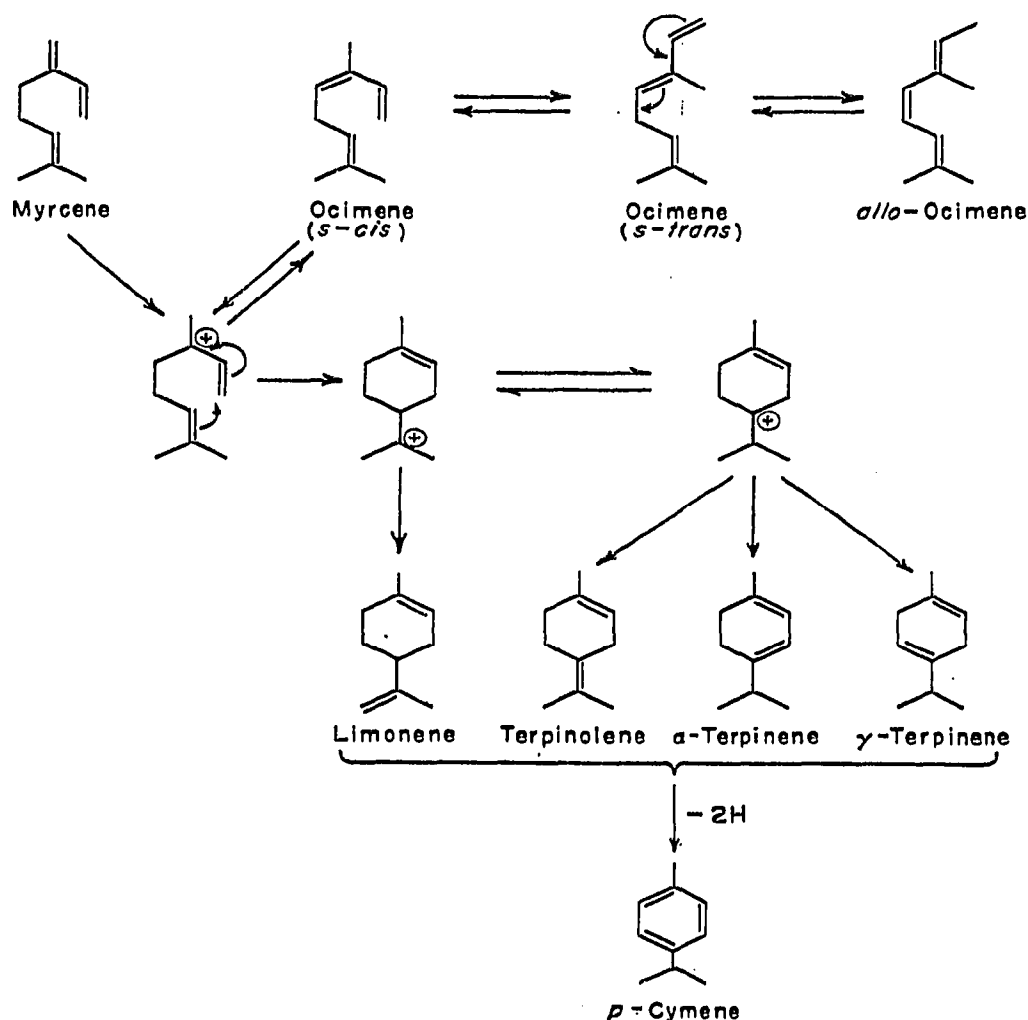

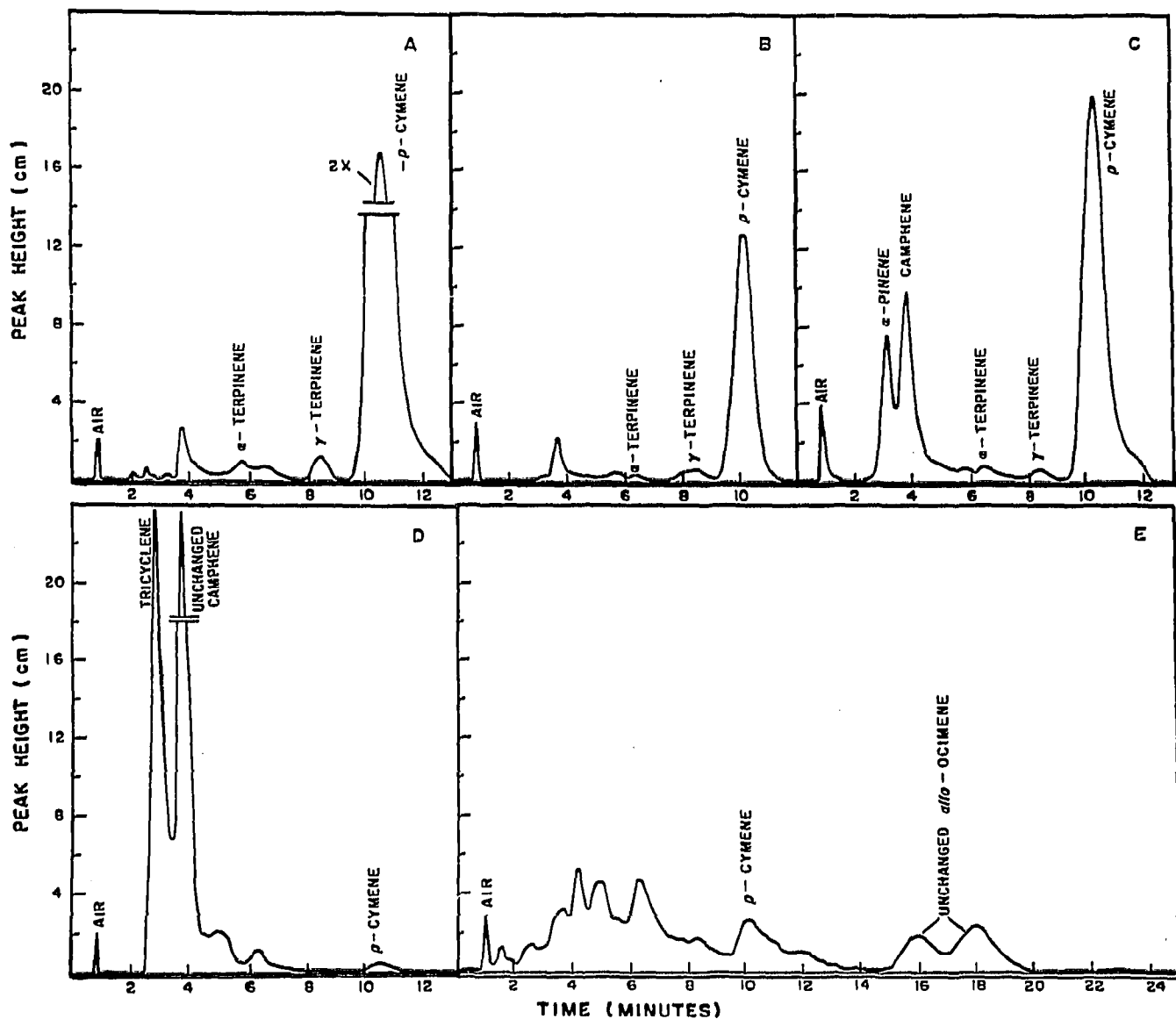Fig. 1. Isomerization and aromatization of acyclic terpenes on Pt–alumina.

Fig. 2. Dehydrogenation gas chromatography of terpene hydrocarbons at 220°. Samples: A = limonene; B = 3-carene; C = β-pinene; D = camphene; E = *allo*-ocimene. Column temperature: 110° ± 1°. Carrier gas: helium, 75 ml/min.

TABLE II

DEHYDROGENATION GAS CHROMATOGRAPHY OF TERPENE HYDROCARBONS AT 150°

No.	Hydrocarbon	Main products of reaction (%)		
		α-Terpinene	γ-Terpinene	p-Cymene + terpinolene
1	α-Phellandrene	31	8	53
2	Limonene	40	12	40
3	Terpinolene	33	8	55
4	Sabinene	40	11	42
5	3-Carene*	13	3	72
6	β-Pinene	20	5	27
7	Myrcene	19	4	51

* Yielded 7 % of uncharacterised product (relative retention time: 1.33; reference: p-cymene).

produced significant quantities of α-terpinene and γ-terpinene. At 125° limonene was also detected. Varying amounts of terpinolene were produced at 125° as well as 150° (Tables II and III). Typical dehydrogenation gas chromatograms are shown in Figs. 2 and 3. On the Reoplex 400 column both terpinolene and p-cymene emerged together but the two compounds appeared as well resolved peaks when the effluent fraction was rechromatographed on an SE-30 column. When the reactor was operated at 220° only small quantities of α-terpinene and γ-terpinene were formed. The presence of terpinolene amongst the products of reaction was observed only in the case of sabinene (see Table I). Evidently, limonene, terpinolene, α-terpinene and γ-terpinene formation are intermediate stages in the aromatization of the terpenes examined (Fig. 4).

The observation that limonene was formed only at 125° confirmed that this monoterpene is more unstable than terpinolene[5]. At 125° ocimene was almost completely converted to allo-ocimene, which itself remained unaffected at this temperature.

The molecular rearrangements which accompanied the dehydrogenation reaction are of particular interest. Isomerisation of ocimene to allo-ocimene and formation of carvomenthene from 3-menthene were described previously (see Table I). α-Pinene gave camphene through Wagner-Meerwein rearrangement. β-Pinene yielded both α-pinene and camphene. Camphene was cyclized to tricyclene. Presumably these rearrangements take place under the influence of alumina which possesses some intrinsic acidity[6]. Disproportionation reactions during dehydrogenation, frequently reported in the literature[7], were not observed to any significant extent. Only minor

TABLE III

DEHYDROGENATION GAS CHROMATOGRAPHY OF TERPENE HYDROCARBONS AT 125°

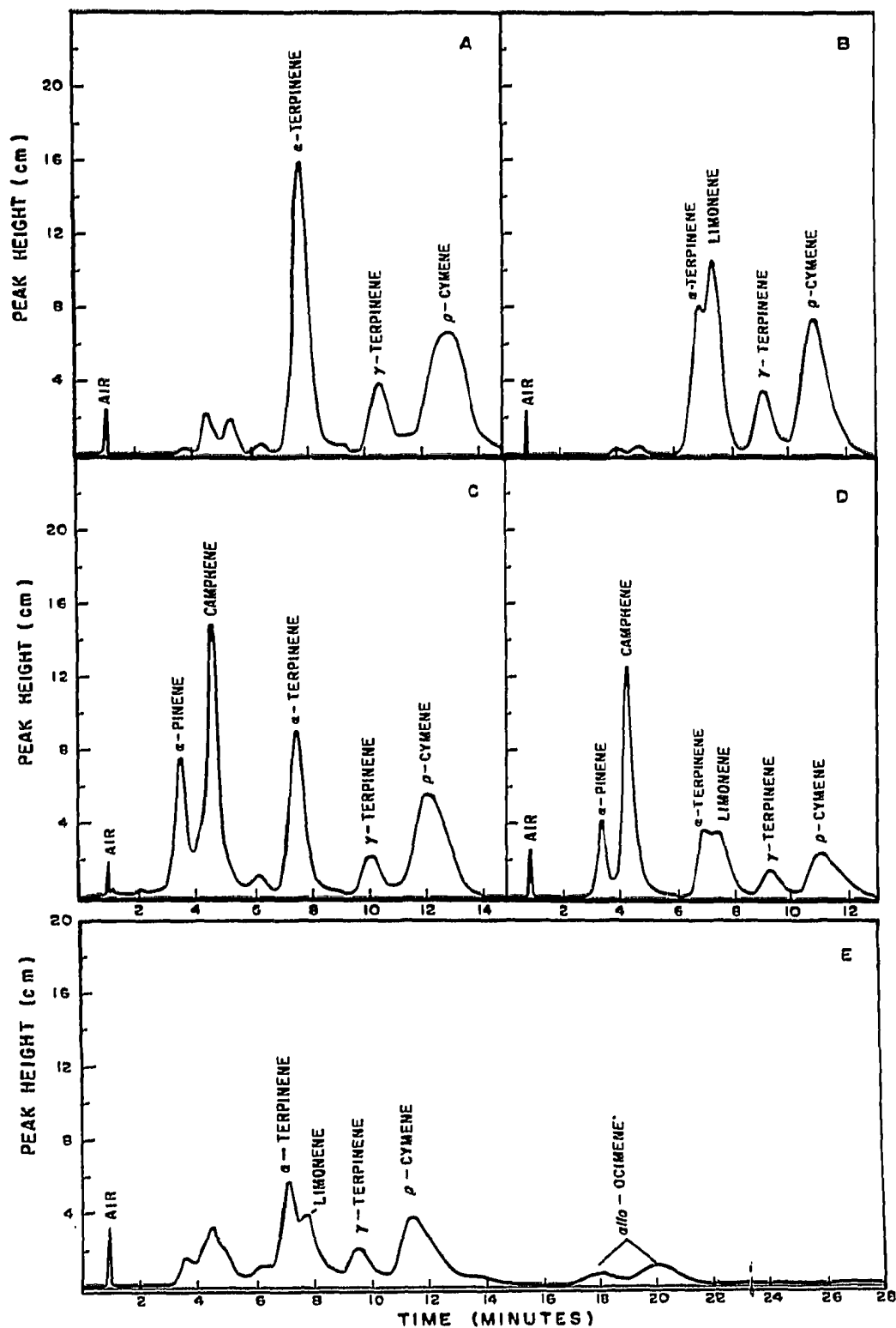| No.	Hydrocarbon	Main products of reaction (%)		
		α-Terpinene + limonene	γ-Terpinene	p-Cymene + terpinolene
1	Limonene	49	12	38
2	β-Pinene	27	7	18
3	Myrcene*	31	8	26

* Partly converted to allo-ocimene (12 %).

Fig. 3. Dehydrogenation gas chromatography of terpene hydrocarbons at 150° and 125°. Samples: A and B = limonene; C and D = β-pinene; E = myrcene. Reactor temperatures: A and C, 150°; B, D and E, 125°. Column temperature: 110° ± 1°. Carrier gas: helium, 75 ml/min.
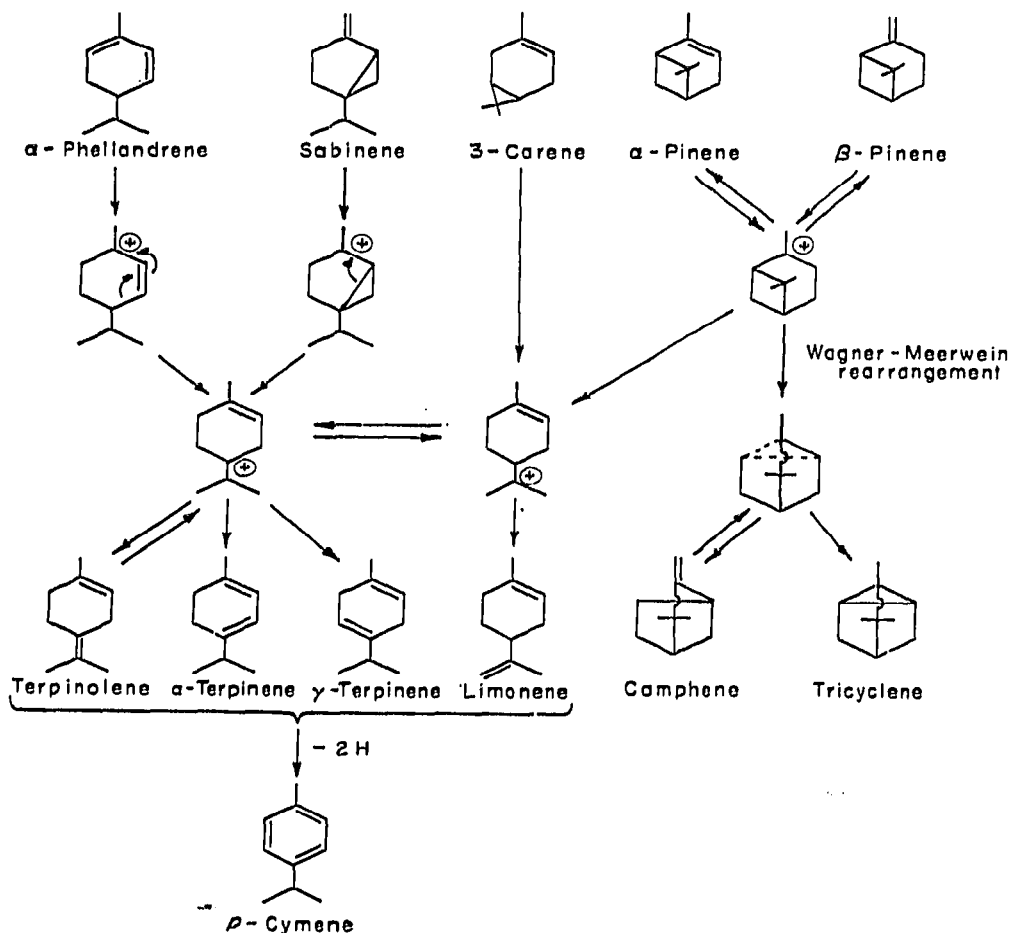
Fig. 4. Isomerization and aromatization of cyclic terpenes on Pt/alumina.

peaks eluting at the same retention times as *cis-* and *trans-p*-menthane were observed in some cases, but their identity could not be confirmed.

Alcohols

Dehydrogenation of alcohols appeared to proceed *via* the corresponding hydrocarbons formed by dehydration. The nature of the intermediate hydrocarbons, isolated in some cases, determined the extent to which aromatization occurred. Experimental results are summarized in Table IV and some typical reaction gas chromatograms shown in Fig. 5.

Monocyclic alcohols possessing a *p*-menthane framework and a double bond in the ring, *e.g.* carveol, isopiperitenol and α-terpineol readily dehydrogenated at 150° yielding *p*-cymene and α- and γ-terpinenes. Terpene alcohols possessing saturated rings, *e.g.* dihydrocarveol and isopulegol failed to decompose appreciably at 150° and gave only small quantities of *p*-cymene. At 220°, however, they yielded 90 % and 50 % of *p*-cymene, respectively. Menthol gave a low yield of *p*-cymene (5 %). It was largely converted into 3-menthene, some of which isomerised to carvomenthene. The bicyclic alcohols β-fenchol and borneol showed little tendency to aromatize. They yielded dehydration products along with the expected products of rearrangements. Thus, at 150° β-fenchol gave cyclofenchene, camphene and traces of *p*-cymene.
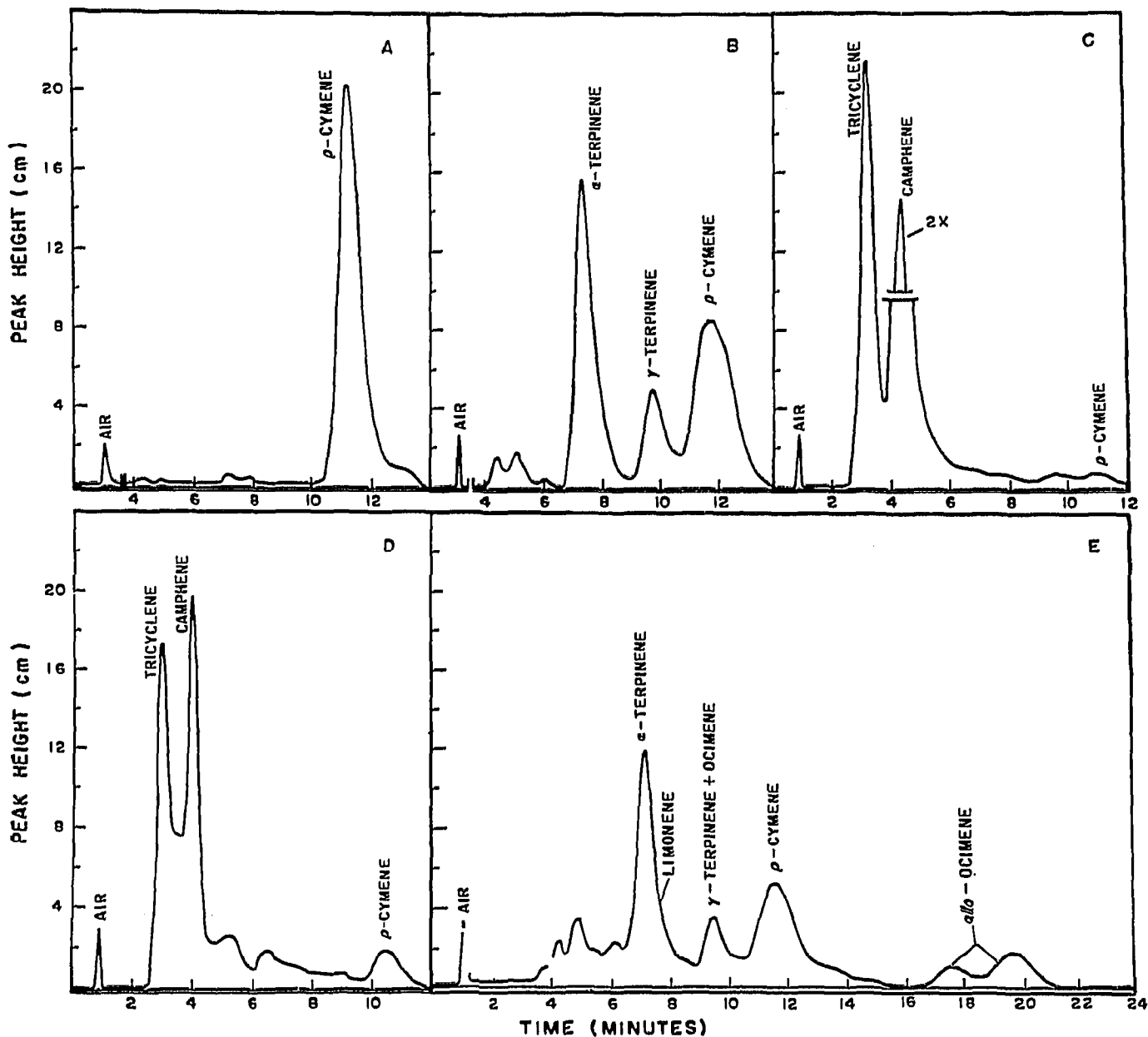
Fig. 5. Dehydrogenation gas chromatography of terpene alcohols. Samples: A = isopiperitenol; B = α-terpineol; C = β-fenchol; D = borneol; E = linalool. Reactor temperatures: A, B, C and E, 150°; D, 220°. Column temperature: 110° ± 1°. Carrier gas: helium, 75 ml/min.

TABLE IV

DEHYDROGENATION GAS CHROMATOGRAPHY OF TERPENE ALCOHOLS

No.	Compound	Temperature of reactor (°C)	Main products of reaction*
1	trans-Carveol	150	p-Cymene (50%), α-terpinene (<5%), γ-terpinene (traces)
2	Isopiperitenol	150	p-Cymene (97%)
3	α-Terpineol	150	p-Cymene (40%), α-terpinene (40%), γ-terpinene (13%)
4	Dihydrocarveol	220	p-Cymene (90%)
5	Isopulegol	220	p-Cymene (50%)
6	Menthol	220	p-Cymene (5%), 3-menthene (58%), carvomenthene (36%)
7	β-Fenchol	150	p-Cymene (<5%), tricyclene** (30%), camphene (58%)
8	Borneol	220	p-Cymene (9%), camphene (41%), tricyclene (26%)
9	Citronellol	220	p-Cymene (<5%), and unidentified low boiling compounds
10	Geraniol	150	p-Cymene (30%), limonene and α-terpinene (20%), γ-terpinene*** (6%), allo-ocimene (20%)
11	Linalool	150	p-Cymene (30%), limonene and α-terpinene (35%), γ-terpinene*** (12%), allo-ocimene (20%)

* p-Cymene and small amounts of terpinolene emerged as a single peak and have been reported as p-cymene.
** Identified by retention time only.
*** Contains possibly some ocimene.

Borneol, which is usually resistant to dehydration, required a higher temperature of reaction (220°), yielding camphene and tricyclene along with 10% of p-cymene. Citronellol, possessing a hydroxyl group and double bond at isolated positions, remained practically unaffected at 150°.. At 220°, however, it degraded yielding several unidentified low boiling compounds and a small quantity of p-cymene. Because of the presence of two olefinic linkages, geraniol and linalool cyclised and dehydrogenated readily, each yielding α-terpinene, γ-terpinene, limonene, p-cymene and allo-ocimene. These hydrocarbons may be visualized to form by different modes of stabilization of the mesomeric ions generated under the influence of alumina (Fig. 6).

Esters

Reactions of terpene esters were similar to those of the terpene alcohols. The compounds readily lost a molecule of acid and the hydrocarbons formed rearranged and aromatized yielding the same products as the corresponding alcohols. They re-
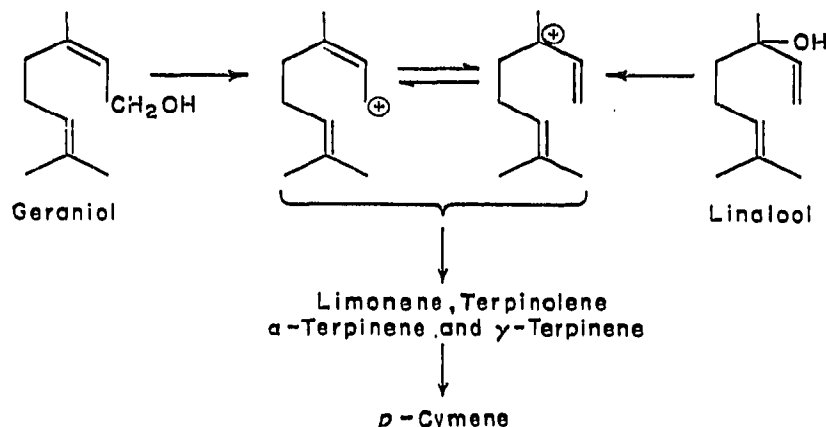

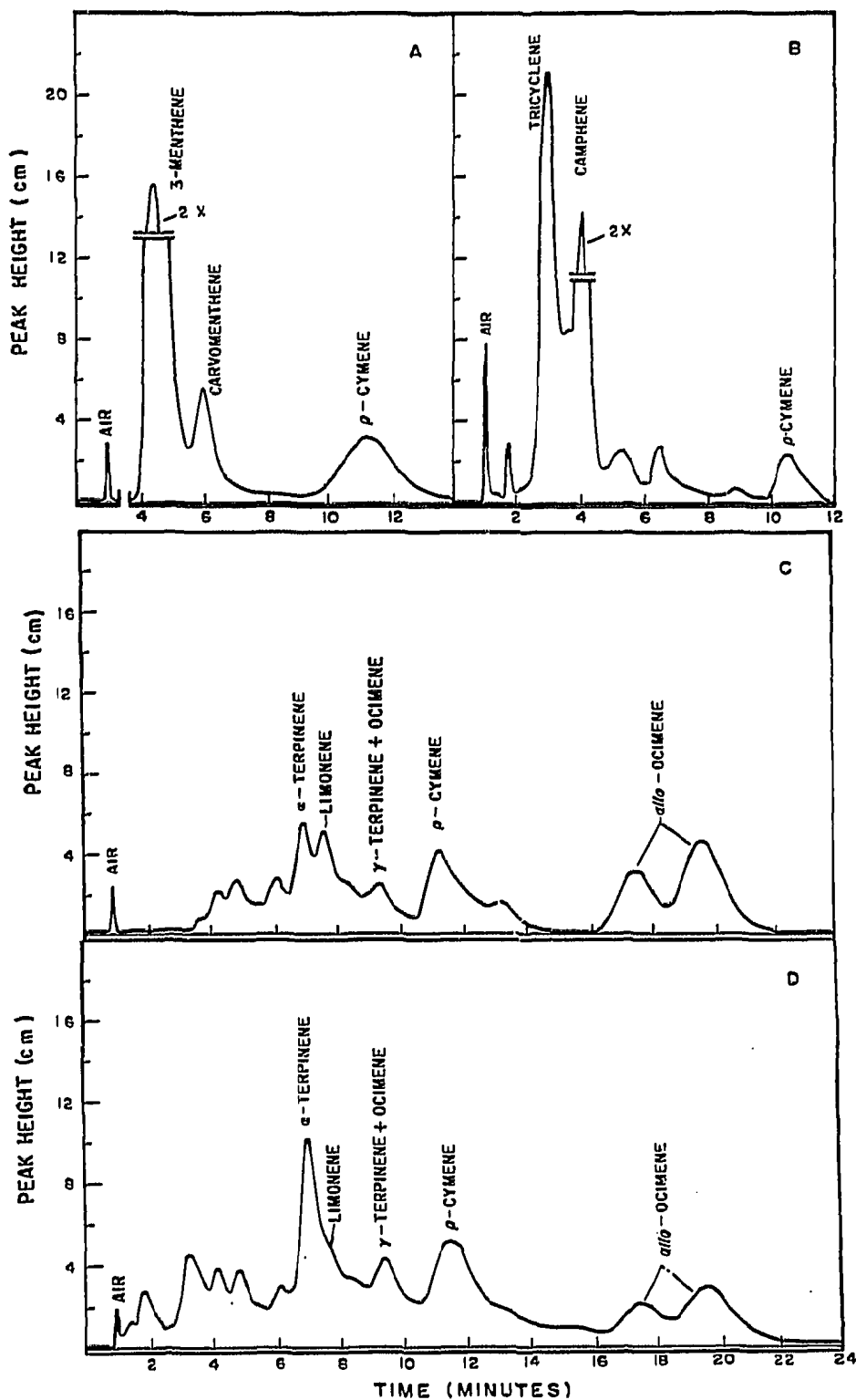Fig. 6. Cyclization and aromatization of geraniol and linalool.

Fig. 7. Dehydrogenation gas chromatography of terpene esters. Samples: A = menthyl acetate; B = bornyl acetate; C = linalyl acetate; D = linalyl formate. Reactor temperature: 150°. Column temperature: 110° ± 1°. Carrier gas: helium, 75 ml/min.

TABLE V

REACTION GAS CHROMATOGRAPHY OF TERPENE ESTERS AT 150°

No.	Compound	Main products of reaction*
1	*trans*-Carveyl acetate	*p*-Cymene (90 %), α-terpinene (< 5 %), γ-terpinene (5 %)
2	Dihydrocarveyl acetate	*p*-Cymene (32 %), limonene and α-terpinene (43 %), γ-terpinene (13 %)
3	Menthyl acetate	*p*-Cymene (15 %), 3-menthene (70 %), carbomenthene (15 %)
4	Bornyl acetate	*p*-Cymene (traces), camphene (68 %), tricyclene (22 %)
5	Geranyl acetate	*p*-Cymene (13 %), limonene and α-terpinene (19 %), γ-terpinene** (< 5 %), *allo*-ocimene (27 %)
6	Linalyl acetate	*p*-Cymene (16 %), γ-terpinene** (6 %), limonene and α-terpinene (24 %), *allo*-ocimene (33 %)
7	Geranyl formate	*p*-Cymene (19 %), limonene and α-terpinene (21 %), γ-terpinene** (5 %), *allo*-ocimene (30 %)
8	Linalyl formate	*p*-Cymene (24 %), limonene and α-terpinene (33 %), γ-terpinene** (9 %), *allo*-ocimene (12 %)

   * *p*-Cymene and small amounts of terpinolene emerged as a single peak and have been reported as *p*-cymene.
   ** Contains possibly some ocimene.

quired a lower reaction temperature than the corresponding alcohols. Table V summarises the results obtained and typical gas chromatograms are shown in Fig. 7.

Aldehydes and ketones

Most of the aldehydes and ketones included in this study remained unaffected under the experimental conditions. Some aldehydes are known to lose a carbon atom as carbon monoxide under conditions of dehydrogenation[8,9] but during the present investigation no such reaction was observed. Citronellal remained practically unaffected even at 220°, whereas citral yielded 90 % of *p*-cymene at 150°. Six-membered ring ketones are often converted into phenols during dehydrogenation, *e.g.* menthone and pulegone to thymol and carvone to carvacrol[10]. Such reactions were likewise, not observed. Carvone, dihydrocarvone, menthone, isomenthone and piperitone remained unaffected at 150° yielding only traces of *p*-cymene at 220°. Thujone, on the other hand, gave 10 % and 50 % of *p*-cymene at 150° and 220°, respectively.

Scope of the technique

The experimental results reported demonstrate that dehydrogenation of terpenoids can be efficiently carried out on a micro scale *via* reaction gas chromatography. The technique permits meaningful correlations of reaction products and molecular structure. Its value in the analysis and characterization of sesquiterpene compounds is to be demonstrated in a forthcoming publication from this laboratory[11].

SUMMARY

Dehydrogenation of forty-two monoterpenes was investigated *via* "reaction gas chromatography" employing a reactor packed with 5 % platinum on alumina. Products obtained were analysed and experimental data correlated to the structures of the parent compounds. The technique should prove of value in the identification and structure elucidation of terpenoids. Mechanisms of dehydrogenations and isomerisations involved have also been discussed.

REFERENCES

1 I. C. NIGAM, *J. Chromatog.*, 24 (1966) 188.
2 T. OKAMOTO AND T. ONAKA, *Chem. Pharm. Bull. (Tokyo)*, 11 (1963) 1086.
3 I. C. NIGAM AND L. LEVI, *Can. J. Chem.*, 40 (1962) 2083.
4 W. KLYNE, *Progress in Stereochemistry*, Vol. I, Butterworths, London, 1954, p. 137.
5 G. W. GLADDEN AND G. WATSON, *Perfumery Essent. Oil Record*, 55 (1964) 793.
6 H. PINES AND W. O. HAAG, *J. Am. Chem. Soc.*, 82 (1960) 2471.
7 Z. VALENTA, in A. WEISSBERGER (Editor), *Techniques of Organic Chemistry*, Vol. XI, *Elucidation of Structures by Physical Chemical Methods*, Part I, Interscience, New York, 1963, p. 596.
8 H. E. ESCHINAZI, *Bull. Soc. Chim. France*, (1952) 967.
9 M. S. NEWMAN AND T. S. BYE, *J. Am. Chem. Soc.*, 74 (1952) 905.
10 R. P. LINSTEAD, K. O. A. MICHAELIS AND S. L. S. THOMAS, *J. Chem. Soc.*, (1940) 1139.
11 I. MIZRAHI, I. C. NIGAM AND L. LEVI, unpublished studies.