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STUDIES ON THE COMPOSITION OF THE ESSENTIAL OILS OF THREE *NEPETA* SPECIES*†

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Abstract—The composition of the essential oils produced by *Nepeta cataria*, *N. citriodora* and *N. mussini* was determined using gas chromatography–mass spectrometry with open tubular columns. All of the *Nepeta* species studied produced nepetalactone, epinepetalactone, and caryophyllene. Only *N. cataria* formed camphor while only *N. citriodora* produced citronellol, geraniol, citral, and neral. The species studied may be easily recognized by the major constituent of their essential oils. Over 77 per cent of the essential oil of *N. cataria* was nepetalactone while 70 per cent of the essential oil of *N. mussini* was epinepetalactone. The major volatile constituent of *N. citriodora* was citronellol. The nepetalactone: epinepetalactone ratio in *N. cataria* is almost reversed in *N. mussini*. Many minor components remain to be identified in each of the oils.

INTRODUCTION

Nepeta cataria L., commonly known as catnip, produces the feline attractant nepetalactone along with a number of other volatile compounds. The function of secondary plant substances such as nepetalactone has never been satisfactorily explained. However, Fraenkel[1,2] has demonstrated that in a number of plants these substances may function as insect attractants and repellants. Eisner[3] has reported that nepetalactone is a repellant to several insects.

Our studies[4] with the essential oils of three *Nepeta* species have indicated that ants are strongly repelled from their natural food by these oils. In the identification of the biologically active components, a more precise knowledge of their composition was a prerequisite. This paper describes studies on the composition of the essential oils of *N. cataria*, *N. mussini*, and *N. citriodora*.

RESULTS

The essential oils obtained from steam distilling *Nepeta cararia*, *N. citriodora* and *N. mussini* account for 0·2, 0·6, and 0·1 per cent|| respectively of the freshly harvested tops of these plants. Since the roots of these plants produced very little volatile material, they were not

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|| These values may vary as much as ± 50 per cent between individual plants.

[1] G. FRAENKEL, J. K. MAYAR, O. NALBANDOV and R. T. YAMAMOTO, *Proc. 11th Intern. Congr. Entomol.*, Vienna, Vol. 3, p. 122 (1960).

[2] G. FRAENKEL, *Science* **129**, 1466 (1959).

[3] T. EISNER, *Science* **148**, 1218 (1965).

[4] K. VICK, F. E. REGNIER, G. R. WALLER, W. A. DREW, E. J. EISENBRAUN. In preparation.

processed. An analysis of *N. cataria* roots showed the concentration of nepetalactone (Fig. 1 (Ia)), caryophyllene (VI) and humulene (VII) to be about one-millionth of that in the leaves and stems. Maximum yields of essential oil were obtained by harvesting plants during the flowering stage; consequently, only mature flowering plants were used in this study.

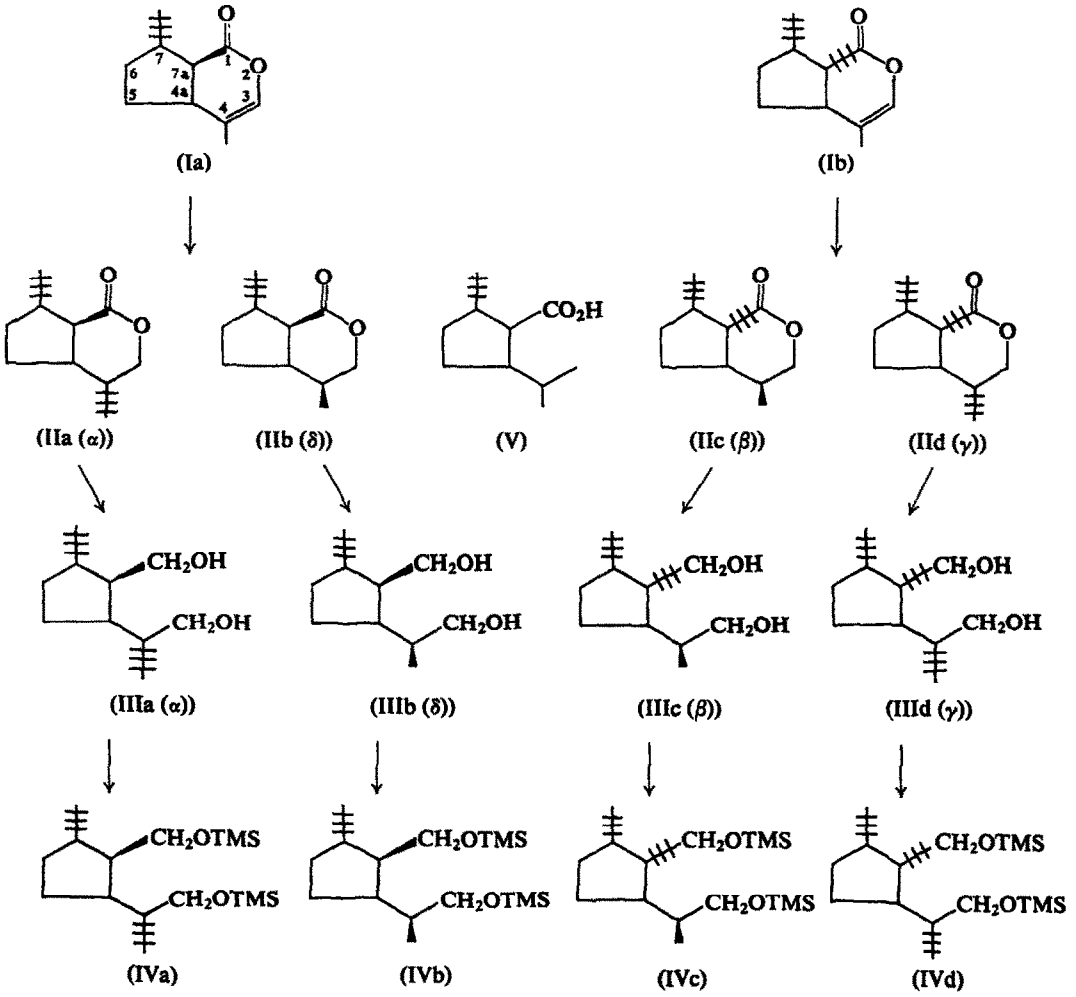
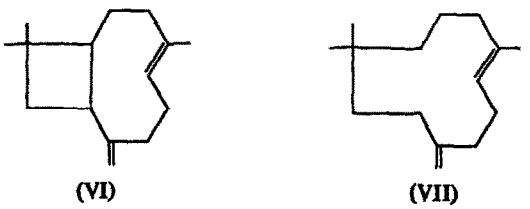


FIG. 1. CHEMICAL DEGRADATION OF NEPETALACTONE (Ia) AND EPINEPETALACTONE (Ib) TO YIELD THE CORRESPONDING NEPETADIOLS. NEPETALACTONE YIELDS THE α-NEPETADIOL (IIIa) AND δ-NEPETADIOL (IIIb), AND EPINEPETALACTONE YIELDS THE β-NEPETADIOL (IIIc) AND γ-NEPETADIOL (IIId).



The three essential oil samples were gas chromatographed on a six-ring polyphenyl ether open tabular column, and the results are shown in Fig. 2. An Apiezon L open tubular column was also used for comparison of mass spectrometry–gas chromatography (MS–GC) characteristics.[5] Compounds in these mixtures have been identified as indicated on the chromatograms. The results obtained from analyzing the three oils using the two GLC columns and the

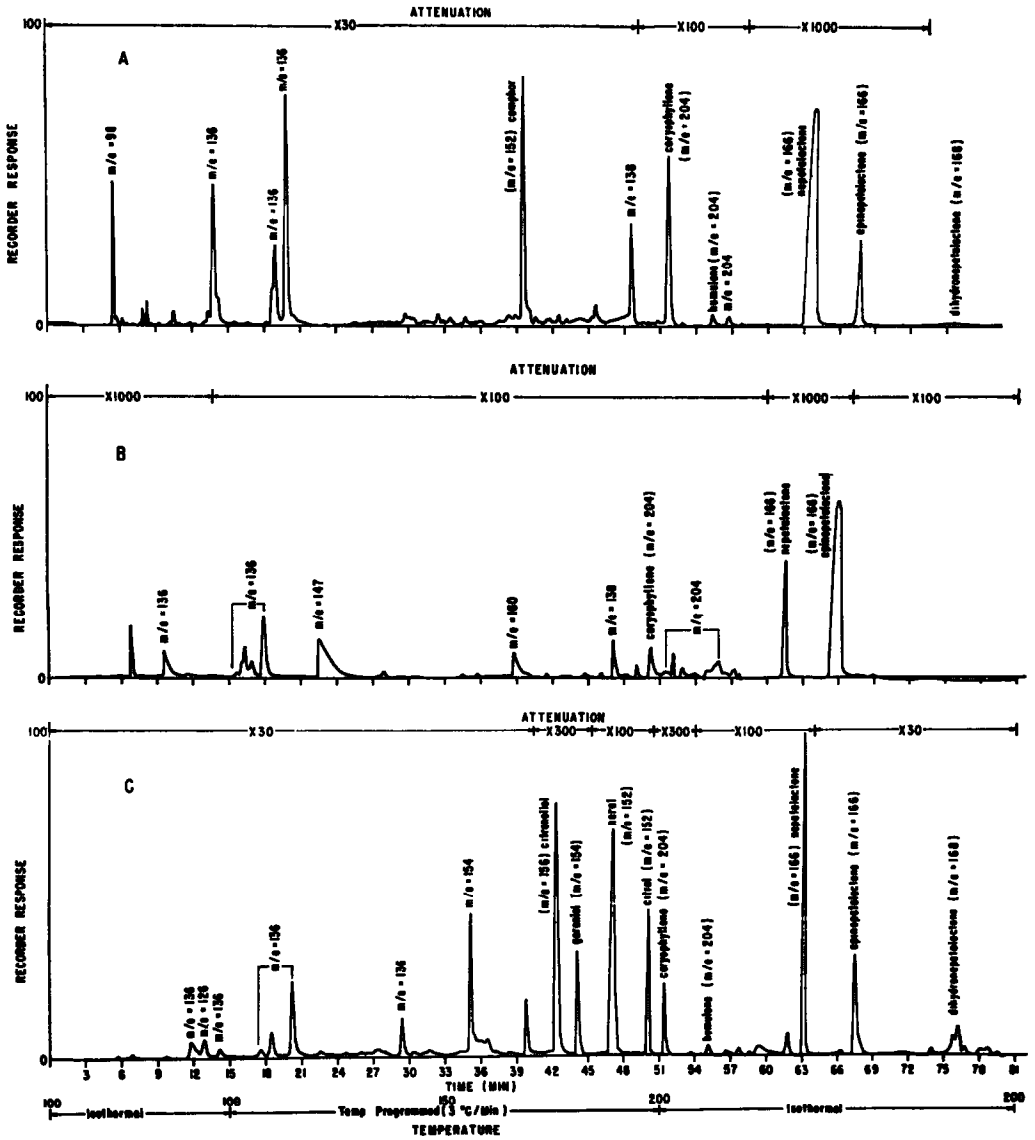


FIG. 2. GAS–LIQUID CHROMATOGRAPHY OF *Nepeta cataria* OIL (A), *N. mussini* OIL (B) AND *N. citriodora* OIL (C).

0·05 μl samples were injected on a 500 ft × 0·02 in. OS-138 polyphenyl ether column. The hydrogen flame detector was kept at 200° and the injection port at 150°. The helium pressure was 25 psi. The attenuation settings and programming conditions for the column are shown on the figure.

[5] F. E. REGNIER, E. J. EISENBRAUN and G. R. WALLER, *Phytochem.* 6, 1271 (1967).

parent mass of each compound found are shown in Table 1. The compounds in these samples will be discussed as groups: lactones, ketones and aldehydes, alcohols, and hydrocarbons. In each case, identifications were made based on the similarity of retention times with those of reference compounds on the polyphenyl ether column and on comparison of the mass spectrum of the unknown and of a reference compound. For certain compounds, chemical degradation was used also.

TABLE 1. CONSTITUENTS OF THE ESSENTIAL OILS OBTAINED FROM *Nepeta cataria*, *N. mussini* AND *N. citriodora*

m/e	Compound	Yield, per cent[a]			Relative retention time[b]
		N. cataria	*N. mussini*	*N. citriodora*	
98		0·3	—	—	0·09
136		0·7[c]	—	—	0·22
136		0·4[c]	—	—	0·30
136		1·0[c]	—	—	0·31
136		—	5·9	—	0·16
136		—	2·0[d]	—	—
147		—	2·1	—	0·37
136		—	—	0·3	0·19
126		—	—	0·2	0·20
136		—	—	0·1	0·22
136		—	—	1·8[e]	—
136		—	—	0·6	0·46
154		—	—	1·6	0·56
160		—	0·7	—	0·63
152	Camphor	0·8	—	—	0·62
156	Citronellol	—	—	48·3	0·67
154	Geraniol	—	—	13·7	0·70
152	Neral	—	—	4·9	0·75
138		0·4	0·3	—	0·76
152	Citral	—	—	5·6	0·79
204	Carophyllene	2·8	0·3	8·0	0·81
204		—	1·6[f]	—	—
204	Humulene	0·3	—	0·1	0·87
204		0·2	—	—	0·89
166	Nepetalactone	77·6	16·7	9·4	1·0
166	Epinepetalactone	15·0	70·0	1·6	1·07
168	Dihydronepetalactone	0·3	—	1·2	1·20

[a] Compounds present in a concentration of less than 0·1 per cent are not reported.
[b] Relative retention time in minutes as compared to nepetalactone.
[c] Includes "shoulders" in Fig. 2A which are also m/e = 136.
[d] Refers to bracketed peaks in Fig. 2B with m/e = 136.
[e] Refers to bracketed peaks in Fig. 2C with m/e = 136.
[f] Refers to bracketed peaks in Fig. 2B with m/e = 204.

Lactones

Nepetalactone (Ia) (m/e = 166) was isolated from *N. cataria* oil by preparative gas chromatography and its identity proven by both oxidation to the corresponding nepetalinic acids[5] and $LiAlH_4$ reduction to the α- and δ-nepetadiols (Fig. 1 (IIIa) and (IIIb)). The treatment of (Ia) with hydrogen and platinum oxide catalyst yielded both hydrogenation and hydrogenolysis products (Fig. 1). The principal hydrogenolysis product was an acid (V) which was structurally but not stereochemically characterized by Meinwald.[6] The hydrogenation prod-

[6] J. MEINWALD, *J. Am. Chem. Soc.* 76, 4571 (1954).

ucts were a pair of lactones (IIa and IIb) which are stereochemically related to the α- and δ-nepetalinic acids.[7,8] Since the carbon skeletons of these compounds are structurally and stereochemically identical, the names α-dihydronepetalactone (IIa) and δ-dihydronepetalactone (IIb) are proposed. In the hydrogenation of (Ia) with platinum catalyst, yields of 53 per cent of (V), 2·8 per cent of (IIa), and 35 per cent of (IIb) were obtained. When palladium catalyst supported on strontium carbonate was used, 90 per cent (IIa), 3 per cent (V), and a trace of (IIb) were formed. The stereochemistry of (IIa) and (IIb) was established by reducing them with $LiAlH_4$ to the corresponding nepetadiols (IIIa and IIIb). The four diols (IIIa), (IIIb), (IIIc), and (IIId) were identified by analysis on two different gas chromatography columns. The α- and δ-isomers had identical retention times (22 min). The β- and γ-isomers also had identical retention times (26 min) on an Apiezon L column (Table 2). However, these two isomeric pairs were differentiated by gas chromatographic analysis of their trimethylsilyl (TMS) derivatives on Carbowax 20M.

TABLE 2. GAS CHROMATOGRAPHIC RETENTION TIMES OF THE NEPETADIOLS AND THEIR TRIMETHYLSILYL DERIVATIVES

Compound	Retention time (min)	
	Free diol on Apiezon L[a]	TMS derivative on Carbowax 20 M[b]
α-Nepetadiol	22	15·8
δ-Nepetadiol	22	17·2
β-Nepetadiol	26	17·2
γ-Nepetadiol	26	18·5

[a] Conditions: 24 ft × ¼ in. Pyrex glass column, 25% Apiezon L on 80/100 mesh Gas-Chrom Q; 200°, 60 ml/min helium flow.
[b] Conditions: 20 ft × ¼ in. Pyrex glass column, 3% Carbowax 20 M on 80–100 mesh Gas-Chrom Q; 130°, 80 ml/min helium flow.

Nepetalactone (Ia) was present in amounts varying from 9 per cent to 78 per cent in all of the *Nepeta* species examined as shown in Table 1. This compound has been reported as a constituent of *N. cataria* oil previously[7,9,10] but has not previously been reported to occur in *N. mussini* or *N. citriodora* oils.

Epinepetalactone (Ib) (m/e = 166) was isolated from *N. mussini* by preparative gas chromatography because of its abundance in these plants (Table 1). Mass spectral data[5] and chemical degradation (Fig. 1) of this compound indicated that it was an epimer of nepetalactone (Ia). This epimer was named epinepetalactone in a previous paper[5] and has been previously reported to occur in *N. cataria*.[7,9,10] Catalytic hydrogenation with platinum involves both addition of hydrogen and cleavage in much the same manner as with nepetalactone (Ia). Two lactones (IIc and IId) (m/e = 168) were formed in 8·5 epr cent and 24 per cent yield. Reduction of these lactones with $LiAlH_4$ produced β- and γ-nepetadiols (IIIc and IIId). These results

[7] S. M. MCELVAIN and E. J. EISENBRAUN, *J. Am. Chem. Soc.* 77, 1599 (1955).
[8] E. J. EISENBRAUN, A. BRIGHT and H. H. APPEL, *Chem. Ind.* 1242 (1962).
[9] R. B. BATES and C. W. SIGEL, *Experentia* 19, 564 (1963).
[10] T. SAKAN, S. ISOE, S. B. HYEON, R. KATSUMURA, T. MAEDA, J. WOLINSKY, D. DICKERSON, M. SLABAUGH and D. NELSON, *Tetrahedron Letters* 4097 (1965).

serve to confirm that this compound is epimeric with (Ia) at the 7a ring position. Epinepetalactone (Ib) was found in *N. cataria* and *N. citriodora* also by MS–GC analysis (Table 1).

A third compound with m/e = 166, with a retention time of 66 min, was observed and is shown in the gas chromatogram of *N. citriodora* (Fig. 2C). This component is probably neonepetalactone, described by Sakan *et al.*[10]

Dihydronepetalactone was isolated from *N. cataria* oil by preparative gas chromatography. Mass spectral analysis (m/e = 168) and reduction with $LiAlH_4$ to α-nepetadiol(IIIa) suggested that this compound was a dihydronepetalactone. When subjected to analysis by MS–GC, this compound had the same spectral pattern and retention time as the synthetic (IIa) produced by the catalytic hydrogenation of (Ia) with palladium on strontium carbonate. This compound was first synthesized in pure form and characterized as a delta lactone by Eisenbraun.[11] The stereochemistry of this compound was established by reduction to (IIIa), which was analyzed as described previously (Table 2). α-Dihydronepetalactone (IIa) was found to be present in both *N. cataria* and *N. citriodora* oil by combination MS–GC analysis.

When the dihydronepetalactone fraction from *N. cataria* oil was purified by preparative TLC and then subjected to analysis by the combination mass spectrometer–gas chromatograph (MS-GC), a second dihydronepetalactone was observed which corresponded in MS–GC characteristics to the (IIIb) obtained on catalytic hydrogenation of (Ia) with platinum. This lactone was not found initially because of its low concentration (0·02 per cent) in the essential oil. Since the quantities of this second lactone present in the essential oil were so small, it was not possible further to characterize it chemically. It is concluded on the basis of the MS–GC analysis that this second compound with m/e = 168 was (IIb). Sakan *et al.*[10] recently reported similar conclusions concerning the structures of these dihydronepetalactones (IIa and IIb) in commercial oil of catnip.

Aldehydes and Ketones

Citral (m/e = 152) was identified by comparison of its mass spectrum and its retention time on two different columns (Table 1) with those of authentic citral. The base peak in the spectrum of this compound and citral is m/e = 69. This fragment probably results from cleavage of the bond connecting the two isoprene units.[12] *N. citriodora* was the only species which produced this compound.

Another compound from the oil of *N. citriodora* was found to give the same mass spectral fragmentation pattern as citral, but it had a different retention time. However, the GC retention time was identical with that of an impurity in the commercial citral; this impurity also had the same MS fragmentation pattern. From these data, it is probable that this compound is neral, the geometric isomer of citral. This compound probably arises biogenetically from citral.

Camphor was identified by comparing it in MS–GC characteristics with authentic samples on the two gas chromatography columns. The base peak in the spectrum of camphor occurred at m/e = 95 with intense ions also appearing at m/e = 152, 108, 81, and 69. Djerassi and Weinberg[13] have recently proposed a breakdown route for camphor which explains the origin of these fragments. The fragmentation pattern and formation of metastable ions at both 20

[11] E. J. EISENBRAUN, *The Structure of Nepetalic Acid*, Ph.D. Thesis, University of Wisconsin, Madison, Wisconsin (1955).
[12] E. VON SYDOW, *Acta Chem. Scand.* **18**, 1099 (1964).
[13] C. DJERASSI and D. S. WEINBERG, *J. Org. Chem.* **31**, 115 (1966).

and 70 eV agree with the spectra of standard samples and those in the literature.[12,13] *N. cataria* was the only species studied which produced camphor.

Alcohols

The terpene alcohols citronellol and geraniol were identified by comparison of their MS–GC characteristics with those of authentic samples on two different dolumns. The parent ions of these compounds occurred at m/e = 156 and m/e = 154 respectively with the base peak appearing at m/e = 69 in both of these compounds. Their hydroxyl groups are revealed by the occurrence of m/e = $M^+ - 18$. *N. cataria* oil produces predominantly citronellol. The ratio of citronellol to geraniol is 3:5.

An unknown compound has been classified as an alcohol because of the presence of a large peak in the spectrum at m/e = $M^+ - 18$. The parent ion occurs at m/e = 126. Lack of other instrumental or chemical data prevents further structural elucidation of this alcohol. This compound was found only in the *N. citriodora* oil. The compound with m/e = 154 in *N. citriodora* oil is also an alcohol but has not been identified.

Hydrocarbons

Eleven hydrocarbons which possess a molecular weight of m/e = 136 and two with m/e = 138 were found to occur in the three *Nepeta* species. In view of the general similarities of their spectra, they are most likely monoterpenes.[14,15] A detailed study of this complex monoterpenoid hydrocarbon fraction of these oils is currently being conducted.

The sesquiterpene hydrocarbons caryophyllene (VI) and humulene (VII) both have parent ions at m/e = 204. The major hydrocarbon is caryophyllene in *N. cataria* and *N. citriodora* oils whereas a monoterpene with m/e = 136 is the major hydrocarbon in *N. mussini* oil. Small amounts of several unidentified sesquiterpene hydrocarbons each with m/e = 204 were found in *N. mussini* oil whereas that of the other two species contained small amounts of humulene. Both caryophyllene and humulene were also isolated by preparative GLC. Their mass and NMR spectra agree with those published.[16,17]

Miscellaneous

A compound with m/e = 147 was found in *N. mussini* oil. It is probably a nitrogen-containing compound. A compound with m/e = 98 that occurs in *N. cataria* was also unidentified. Further studies are being carried out to identify these compounds.

DISCUSSION

Since only small amounts of these essential oils were available for study from plants properly classified, it was necessary to analyze most of the minor components of these samples by combination mass spectrometry–gas chromatography. The complexity of these essential oil samples necessitated the use of open tubular columns for resolving the components present in the mixtures.

Conclusive proof that nepetalactone (Ia) and epinepetalactone (Ib) occurred naturally was obtained by degrading these compounds to the corresponding nepetadiols (IIIa, IIIb,

[14] R. Ryhage and E. von Sydow, *Acta Chem. Scand.* **17**, 2025 (1963).
[15] A. F. Thomas and B. Willhalm, *Helv. Chim. Acta* **47**, 175 (1964).
[16] J. Andersson and E. von Sydow, *Acta Chem. Scand.* **18**, 1105 (1964).
[17] S. Dev, *Tetrahedron* **9**, 1 (1960).

IIIc, and IIId).[8] Although degradation of nepetalactone and epinepetalactone to their corresponding dimethyl nepetalinates has been described in an earlier paper,[5] it was more convenient to degrade these lactones to the corresponding nepetadiols in this study, since during the course of this degradation, a series of dihydronepetalactones (IIa, IIb, IIc, and IId) was synthesized. Two of these lactones, α-dihydronepetalactone (IIa) and δ-dihydronepetalactone (IIb), were subsequently found to occur naturally in the essential oils of several *Nepeta* species. The other two new lactones are stereochemically related to β- and γ-nepetalinic acid and have therefore been designated β-dihydronepetalactone (IIc) and γ-dihydronepetalactone (IId). Lactones (IIc) and (IId) were not found to occur naturally. Since the nepetadiol standards (IIIa, IIIb, IIIc, and IIId) used in this study were synthesized from the nepetalinic acids,[7,8] a stereochemical relationship between these various methylcyclopentane monoterpenoids has been established.

The electron-impact fragmentation pattern of the oxygenated methylcyclopentanoids suggests several common decomposition routes. In previous studies,[5] it was found that (Ia), (Ib), and the dimethyl nepetalinates all produced ions at m/e = 95. This has also been found to be true for (IIa), (IIb), (IIc), and (IId) and (IIIa), (IIIb), (IIIc), and (IIId). A more detailed mass spectral study of these and other methylcyclopentane monoterpenoids is currently being conducted, and the results will be reported in a separate publication.

Figure 1 shows that catalytic hydrogenation of (Ia) or (Ib) may result in either reduction of the double bond to form lactones (IIa, IIb, IIc, or IId) or hydrogenolysis of the enol lactones to give the acid (V).[6,11] Hydrogenolysis of enol lactones has been previously described.[18,19] The extent of hydrogenolysis or hydrogenation appears to be governed by the type of catalyst used in the reaction. The rate of hydrogenolysis was greater than the rate of hydrogenation when platinum catalyst was used. However, when palladium on strontium carbonate is used, the reaction is directed toward hydrogenation.[11]

The essential oil from all of the *Nepeta* species studied contained (Ia), (Ib), and (VI). *N. cataria* is the only species which contained camphor while *N. citriodora* is the only species which contained citronellol, geraniol, citral, and neral. The species studied may be easily recognized by the major constituent of their essential oils. Over 77 per cent of the essential oil of *N. cataria* was nepetalactone (Ia) while 70 per cent of the essential oil of *N. mussini* was epinepetalactone (Ib). *N. citriodora* produced citronellol as its major volatile constituent. *N. mussini* and *N. cataria* have their nepetalactone (Ia):epinepetalactone (Ib) ratios almost reversed. Many minor components remain to be identified in each of the oils.

METHODS AND MATERIALS

Plant Material

Plants of three *Nepeta* species—*cataria*, *citriodora*, and *mussini*—were grown in the greenhouse of the Department of Horticulture. The plants were harvested at the mature flowering stage of development.

Isolation of the Essential Oils

The technique described previously was used.[5]

Hydrogenation of Nepetalactone and Epinepetalactone

A solution of 0·5 g of the lactone in 5 ml ethanol was stirred with 62 mg of PtO_2 under H_2 at atmospheric pressure. Uptake was usually complete in 1 hr. The filtered concentrate[11] was treated with CH_2N_2, and GLC of the products on a 20 ft × ¼ in. 25% Apiezon column showed yields of 35% δ-dihydronepetalactone, 2·8%

[18] R. L. AUGUSTINE, *Catalytic Hydrogenation*, pp. 64–65. Marcel Dekker, New York (1965).
[19] W. A. JACOBS and A. B. SCOTT, *J. Biol. Chem.* **87**, 601 (1930); **93**, 139 (1931).

α-dihydronepetalactone, and 53% methyl-2-isopropyl-5-methylcyclopentanecarboxylate (V) from nepetalactone.

Lithium Aluminum Hydride Reduction of the Dihydronepetalactones (IIa, IIb, IIc, and IId)

The mixed dihydronepetalactones (50 mg), obtained from the catalytic hydrogenation of nepetalactone (Ia) and epinepetalactone (Ib), in 1 ml of ether were added dropwise to a stirred suspension of 100 mg of $LiAlH_4$ in 2 ml of ether; stirred under reflux for 2 hr, cooled, and saturated Na_2SO_4 added. The product was extracted with ether, dried ($MgSO_4$), filtered and concentrated. The concentrate was analyzed by GLC on the Apiezon L preparative column described below.

Formation of Trimethylsilyl Derivatives

Trimethylsilyl ethers of the nepetadiols (IIIc and IIId) were prepared by dissolving 10 mg of the diol in 1 ml of dry pyridine. To this solution was added 0·1 ml of hexamethyldisilazane and 0·03 ml of trimethylchlorosilane. After standing for 1 hr, the mixture was analyzed directly by GLC on a 3% Carbowax 20 M column.[20]

Thin-layer Chromatography of Dihydronepetalactones

TLC plates (20 × 20 × 0·4 cm) were coated with a 0·5 mm layer of silica Gel-G and activated at 110° for 1 hr. Lactones (IIa) and (IIb) in the mixtures were located by comparison of R_f values with authentic samples. After locating the various components by exposing the plates to iodine vapor, the individual spots were scraped from the plates and eluted from the silica gel with ether.

Preparative Gas Chromatography

All preparative GLC separations were performed on a Perkin-Elmer Model 801 gas chromatograph equipped with a thermal conductivity detector and a Bristol 1-mV recorder. The instrument was fitted with a 7·5 m × 0·8 cm aluminum column packed with 25% Apiezon L on 60–80 mesh Gas Pack P. Samples were collected in 90 × 0·8 cm coiled glass traps.

Gas Chromatography of (IIIa), (IIIb), (IIIc), and (IIId) and Their TMS Derivatives

The nepetadiols were analyzed on the same system as for the preparative separation; trimethylsilyl derivatives of the nepetadiols were chromatographed on a 7·2 m × 0·8 cm glass column packed with 3% Carbowax 20 M on Gas Chrom Q and operated at 125°. Helium at 60 ml/min was used on both columns.

Combination Mass Spectrometric–Gas Chromatographic Analysis of the Essential Oils

MS–GC analyses were performed on the prototype of the LKB model 9000 combination mass spectrometer–gas chromatograph[21,22] equipped with (*a*) a 150 m × 0·5 cm stainless steel open tubular column coated with Monsanto OS-138 (a six-ring polyphenyl ether, bis[m-(m-phenoxyphenoxy)phenyl]ether); and (*b*) a 45 m × 0·05 cm stainless steel open tubular column coated with Apiezon L. The mass spectrometer was operated at an electron energy of 20 eV, accelerator voltage of 3·5 kV, and an ion source temperature of 250°. The molecular separators and injection port were maintained at 150°.

Quantitative estimates of the amount of each compound above 0·1 per cent were made by measuring the area under each peak with a planimeter and computing its percentage of the total area under all peaks. Quantitative analyses were carried out with a modified Barber-Colman Model 5000 gas chromatograph equipped with a hydrogen flame detector.

Reference samples

Samples of caryophyllene and humulene were gifts from The Glidden Company, and camphor, citronellol, geraniol, neral, and citral were obtained from K and K Laboratories.

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[20] M. MAKITA and W. W. WELLS, *Anal. Biochem.* **5**, 523 (1963).
[21] G. R. WALLER, *Proc. Oklahoma Acad. Sci.* **47**, In press.
[22] R. RYHAGE, *Arkiv Kemi*, **26**, 305 (1967).