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Hydrocarbons in Patchouli Oil

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An analytical study of patchouli oil was carried out, and the following compounds were identified; α- and β-pinene, limonene, camphene, β-elemene, caryophyllene, α- and β-patchoulene, α-guaiene, α-bulnesene, allo-aromadendrene, and α-gurjunene. The last six hydrocarbons were hydrogenated in order to complete the identification and to ascertain their spatial configurations by correlating the saturated skeletons with each of these or with known ones.

Commercial patchouli oil is mainly derived from the leaves of *Pogostemon cablin* Benth. (*syn. P. patchouli* Pallet *var. suavis* Hook), which belongs to the Labiatae family and which grows in tropical Asia. The oil is important for compounding perfumery products; its reported components in a sesquiterpene series are β-patchoulene, α-gauiene, α-bulnesene, and patchouli alcohol.[1]

Now that gas chromatographic analysis with a Golay coulmn has revealed the presence of more than ten sesquiterpene hydrocarbons in patchouli oil, a renewed study of the oil has been carried out. The methods were: fractional distillation under diminished pressure for the separation of hydrocarbon fractions; fractional redistillation, gas chromatography, and adsorption chromatography for the final separation of each hydrocarbon; IR, MS, and NMR spectrometry for identification. Some details will be described in the Experimental Section. From the distillation residue, pure patchouli alcohol was separated and dehydrated according to the reported method,[2] thus obtaining authentic α-, β-, and γ-patchoulenes.

Experimental

Material. Patchouli oil (1 kg in one lot) was distilled with Podbielniak's 25-mm × 36-in Heli-Grid column under reduced pressure at a reflux ratio of 10 : 1; nine successive fractions, which, practically speaking, do not contain any oxygenated compounds, were collected. The end temperature was 170°C/23 mmHg at the take-off well; the total amount of the distillate was *ca.* 750 cc. The residue was distilled *in vacuo* to obtain a fraction, 132—135°C/6 mmHg, which was then crystallized from petroleum ether, yielding 84 g of patchouli alcohol, mp. 55—56°C. Each rectified fraction was then again fractionated with a 13 mm × 24-in Heli-Grid column (20 mmHg, $R=1/30$) into several portions with volumes of 2—5 cc. For the final separation, adsorption chromatography or preparative GLC was applied to each fraction of the last fractional distillation. In one case, for a mixture inseparable on an ordinary silicic acid column, modified adsorption chromatography was applied, using silicic acid impregnated with $AgNO_3$.[3]

Adsorption Chromatography. For the separation of the components of the distilled fraction we used Mallinchrodt's silicic acid as an adsorbent in amounts 30—100 times the weight of the sample, and ether in *n*-hexane, in a changing ratio from 0 to 100%, as the elution solvent.

Gas Chromatography. Willkens' Model A-700 (20% CW-20M on chromosorb S, $(3''/8) \times 10'$, 130°C, He) was used for preparative purposes, while Hitachi-Perkin Elmer's Model F-6 (Golay column HB-2000, 150°C, N_2) was used for analysis.

Infrared Spectroscopy. Perkin-Elmer's Infracord Model 137, using a NaCl cell.

Mass Spectrometry. Hitachi's RMU-6 was used; ionizing potential, 80 eV; accelerating potential, 2 kV; ion source temp., 250°C.

Nuclear Magnetic Resonance. Varian's Model A-60 or Jeol's JNM-C-60 was used.

Results and Discussion

Prior to distillation the gas chromatogram of the original oil was obtained in order to check the final analytical results. It is shown on Fig. 1, along with the names of the identified compounds. Monoterpene hydrocarbons are minor constituents; α- and β-pinene, limonene, and camphene, found in the forerun and cold-trap fractions, were identified after gas-chromatographic separation. Among the sesquiterpene hydrocarbons, β-elemene and caryophyllene are widely distributed in nature and, in patchouli oil, have only a minor importance. Therefore, they are omitted in the following discussion.

In Fig. 1, γ-patchoulene is indicated by a dotted line showing its retention time, because it was not present in the orignial oil but was recognized only after distillation. It is well known that patchouli alcohol affords, upon dehydration, α-, β-, and γ-patchoulenes in various ratios according to the

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[1] R. B. Bates and R. C. Slavel, *Chem. & Ind.*, **1962**, 1715.

[2] G. Büchi, R. E. Erickson and N. Wakabayashi, *J. Am. Chem. Soc.*, **83**, 927 (1961).

[3] T. Norin and L. Westfelt, *Acta Chem. Scand.*, **17**, 1828 (1963).

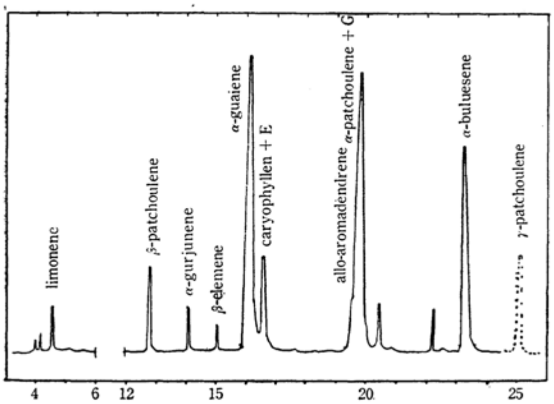
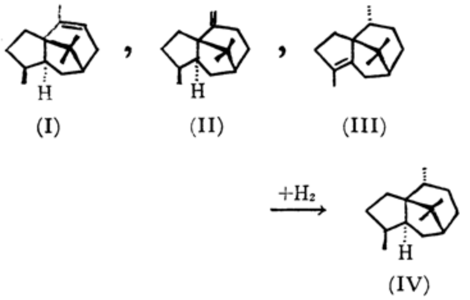


Fig. 1. The gas chromatogram of patchouli oil.

conditions applied.²⁾ Thus, it is more reasonable to consider that α- and β-patchoulenes were present originally in the plants than to consider them as a sign of dehydration during the course of steam-distillation or successive processings to obtain the commercial patchouli oil.

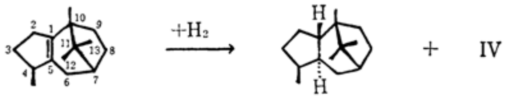
The hydrogenation of α- and γ-patchoulene (I and II respectively) proceeds easily in acetic acid, with platinum oxide as a catalyzer, to afford isopatchoulane (IV). Cyperene (III) is reported also to yield isopatchoulane on hydrogenation,⁴⁾ and all the patchoulanes from these three different hydrocarbons show exactly the same infrared spectrum.



(I) (II) (III) (IV)

Fig. 2.

On the contrary, β-patchoulene (V) was scarcely hydrogenated under the same conditions. Hydrogenation was attained only under a 60-atm pressure of H_2 at 150°C, with platinum oxide in ethanol, for 15 hr, resulting in a mixture of unaltered β-patchoulene (75%), β-patchoulane (VI) (20%), and isopatchoulane (5%).



(V) (VI)

Fig. 3.

This unusual resistance of β-patchoulene to hydrogenation seems to be inherent in the forced trans-addition of hydrogen to the bridge double bond, of which $C_{(5)}$ is hindered by the (12)-methyl group from the β-side and $C_{(1)}$ by the (8, 9)-ethylene bridge from the α-side. The spectral data of β-patchoulane are presented in Fig. 4,

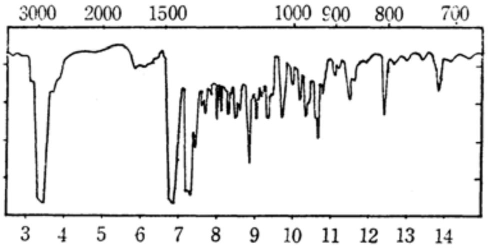


Fig. 4a. The infrared spectrum of β-patchoulane.

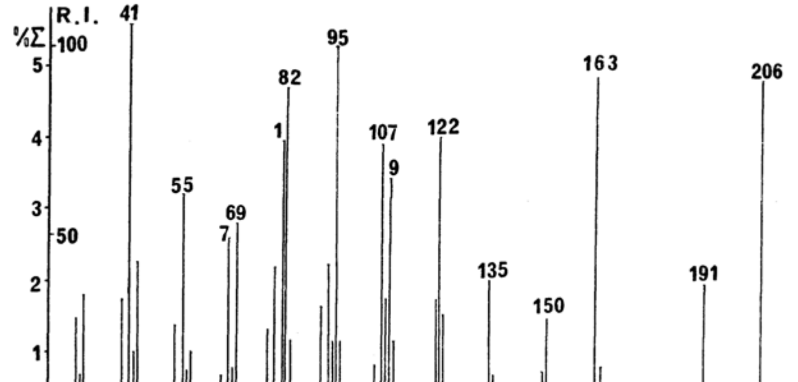


Fig. 4b. The mass spectrum of β-patchoulane.

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4) B. Trivedi, O. Motl, V. Herout and F. Šorm, *Collection Czechoslov. Chem. Communs.*, **29**, 1675 (1964); H. Hikino, K. Aota and T. Takemoto, *Chem. Pharm. Bull.*, **13**, 628 (1965).

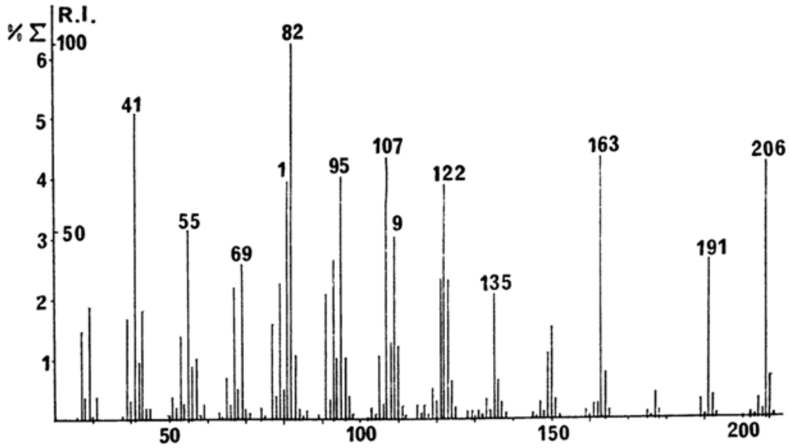


Fig. 4c. The mass spectrum of isopatchoulane.

together with the mass spectrum of isopatchoulane. The mass spectral patterns of β-patchoulane and isopatchoulane are rather similar, except for the *m/e* 82 ion, which is more prominent in the latter (4.7 and 6.3 $\sum\%$ respectively). This may be interpreted as being due to the more favorable bond arrangement in the latter to eliminate the isohexadiene ion.

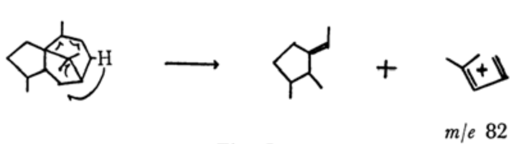
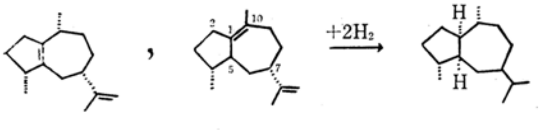


Fig. 5.

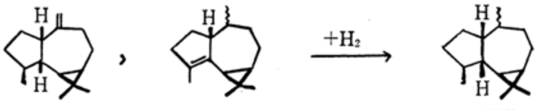
Both α-guaiene (VII) and α-bulnesene (VIII) were easily hydrogenated in an acetic acid solution with platinum oxide to afford guaiane (IX), even though the former has a bridge double bond in the molecule. The identity of α-guaiene was established using an authentic sample of α-guaiene derived from guaiol in guaiac wood oil,⁵⁾ the configuration of which had been thoroughly studied by Minato.⁶⁾ Accordingly, the most probable form of guaiane is expressed by IX, in which the cycloheptane ring should take the boat conformation, less stable in itself. This may be related to the rather lower abundance of M and M-43 ions (2.2 and 5.9 $\sum\%$ respectively) and the higher abundance of *m/e* 109 and *m/e* 95 ions (9.7 and 7.8 $\sum\%$ respectively) of guaiane upon electron impact, compared with other compact bicyclic systems. There remains some obscurity about the orientation of the methyl group on $C_{(10)}$, as the addition of hydrogen atoms to the (1, 10)-double bond of α-bulnesene should result in a β-methyl group on $C_{(10)}$ and bring about some differences in the fragmentation pattern or the infrared spectrum of the guaiane, but such is not the case. This point needs further study.



(VII)　(VIII)　(IX)

Fig. 6.

The hydrogenation of both allo-aromadendrene (X) and α-gurjunene (XI) yields allo-aromadendrane (XII), the identity of which was established by comparing its infrared spectra with those of an issued specimen. Thus, the configuration of α-gurjunene is derived to be as is shown by XI; it is evident that the hydrogen attack was forced from the hindered α-side for, if not, a double folding of the cycloheptane-cyclopropane ring system in the same direction will result in too narrow clearance between one of the *gem*-dimethyl group and an axial hydrogen atom on the cycloheptane ring.



(X)　(XI)　(XII)

Fig. 7.

The orientation of the methyl group on $C_{(10)}$ has not been determined, though it is supposed to be β(equatorial), analogous with the configuration of guaiane. The boat conformation of a cycloheptane ring is thought to be less stable than its chair form; this may be related to the distinct difference in the abundance of molecular ions between aromadendrane and allo-aromadendrane (4.2 and 2.0 $\sum\%$ respectively), the cracking

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5) K. Takeda, H. Minato and S. Nosaka, *Tetrahedron*, **13**, 308 (1961).
6) H. Minato, *ibid.*, **18**, 365 (1965).

patterns of both of which are essentially the same. It is also interesting to note the well-agreed values of the molecular ion abundance between alloaromadendrane and guaiane.

Besides those stated above, several other hydrocarbons were present in patchouli oil, but they have not been identified, as they are minor constituents and are difficult to separate in quantity. Among these, hydrocarbon-E has been defined as a new tricyclic sesquiterpene of mol wt=204 with a tetra-substituted double bond (possibly on a bridge bonding), as the tetranitromethane test was positive and its NMR spectrum showed no absorption below 8.8 τ. The compound was wholely recovered after hydrogenation under a 60 atm. H_2 pressure at 150°C, or by dehydrogenation with paradium charcoal. Another new hydrocarbon, hydrocarbon-G, hidden in the amount of α-patchoulene, was recognized by means of thin-layer chromatography on silicic acid. Its isolation was finally attained by column chromatography on silicic acid impregnated with silver nitrate, though the yield was extremely small. Its spectral characteristics are: (IR) 3080, 890 terminal methylene, and 1210, 1000, 695 cm^{-1}; (NMR) 5.22 and 5.35 τ, 2H, terminal methylene; (MS) M peak *m/e* 204, base peak *m/e* 122. The MS characteristics of hydrogenated hydrocarbon-G are; M peak, *m/e* 206, and base peak, *m/e* 191. In a rare case among saturated skeletons of sesquiterpene hydrocarbons a base peak of M - 15 has been met with; this has been found only in valerane as far as our measurements of thirty-two examples of known compounds are concerned. In view of a possibility of this being a modified skeleton of isopatchoulane, *e. g.,* normal patchoulane, an attempt to isomerise isopatchoulane with anhydrous aluminum chloride is now under way. At present, it seems that the reaction proceeds very rapidly towards adamantane homologs, as the MS pattern of the product exhibits M - 15 and M - 29 concurrently as the most abundant ion species. After all, then, hydrocarbon-G is thought to have an unknown skeleton.