tified component (1%), 2-hexanone (31%), 2-hexanol (5%), 1-methylcyclopentanol (22%), and cyclohexanone (41%).

Reduction of the Methochloride of 7-(1-Piperidino)-2-heptanone (1d).—Lithium (158 mg. or 23 mg.-atoms) was added, portionwise with stirring, to a solution of 2.275 g. (9.2 mmoles) of the salt **1d** in 600 ml. of liquid ammonia until the solution maintained a blue color (indicative of excess lithium) for 15 min. Then the excess lithium was destroyed by the addition of methanol and the ammonia was allowed to evaporate through a 90-cm. Vigreux column. The residue was mixed with saturated, aqueous sodium chloride and extracted with ether. After the ethereal extract had been washed with water, dried, and concentrated, the residual oil (1.132 g.) was found to contain[13] three volatile components: an unidentified component (4%, first eluted), 7-(1-piperidino)-2-heptanone (**8b**, 34%, second eluted), and 7-(1-piperidino)-2-heptanol (**9b**, 62%, third eluted). The latter two samples were identified both by retention times and by comparison of the infrared and mass spectra of collected samples with the spectra of authentic samples.

Reduction of the Methiodide of 6-(1-Piperidino)-2-hexanone (1c).—The preceding experimental procedure was applied to 1.882 g. (5.6 mmoles) of the salt **1c**, 134 mg. (19 mg.-atoms) of lithium and 400 ml. of liquid ammonia being employed. The crude basic fraction, 875 mg. of liquid, contained[13] the following volatile components: an unidentified product (7%, first eluted), 6-(1-piperidino)-2-hexanone (**8a**, 34%, second eluted), and 6-(1-piperidino)-2-hexanol (**9a**, 59%, third eluted). As in the previous case, the products were identified by comparison of retention times, infrared spectra, and mass spectra.

Reduction of the Methiodide of 6-(N,N-Dimethylamino)-2-hexanone (1e).—The previously described reaction and isolation procedure was followed with 2.121 g. (7.5 mmoles) of the salt **1e**, 181 mg. (26 mg.-atoms) of lithium, and 500 ml. of liquid ammonia. The crude, basic product, 784 mg. of liquid, contained[13] three volatile components: A (5%, first eluted), B (17%, second eluted), and C (78%, third eluted). Product B was identified as 6-(N,N-dimethylamino)-2-hexanone (**10**) by comparison of the infrared spectrum of a collected sample with the spectrum of an authentic sample and from its mass spectrum with peaks at *m/e* 143 (M^+), 58 [abundant, $(CH_3)_2N^+{=}CH_2$ and $CH_3(OH)C{=}CH_2^+$], and 43 ($CH_3C{\equiv}O^+$). Component C was tentatively identified as 6-(N,N-dimethylamino)-2-hexanol from the following spectral characteristics of a collected sample. The material has infrared absorption[10] at 3620 and 3400 (broad) cm.$^{-1}$ (unassocd. and assocd. O–H) with n.m.r.[10] singlets at δ 2.62 (1H, OH) and 2.15 (6H, CH_3–N) as well as a doublet (J = 6 c.p.s.) centered at 1.10 (3H, CH_3–) and broad absorption in the regions 3.5–3.9, 2.1–2.4, and 1.3–1.6. The mass spectrum has peaks at *m/e* 145 (M^+), 130 (M^+-CH_3), 58 [abundant, $(CH_3)_2N^+{=}CH_2$], 45 ($CH_3CH{=}O^+H$), and 44 ($CH_3N^+H{=}CH_2$).

Essential Oils and Their Constituents. XXVI.[1] Rearrangement of Caryophyllene Oxide during Gas Chromatography

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The application of chemical and instrumental methods of analysis to essential oils and their constituents requires discriminating interpretation of experimental results. In a previous paper the authors reported the transformation of humulene monoxide, a constituent of oil of wild ginger, to the corresponding alcohol during column chromatography over grade I alumina.[2] It is the purpose of this communication to describe an interesting rearrangement taking place during gas chromatography of caryophyllene oxide, a terpenoid occurring in a number of commercially important essential oils.

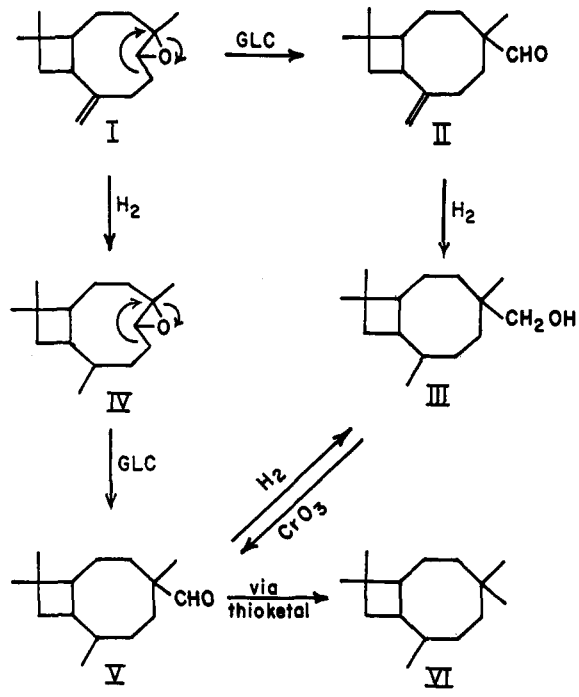

Figure 1.—Rearrangements and transformations of caryophyllene oxide and dihydrocaryophyllene oxide.

The transformation of caryophyllene oxide to compounds possessing novel carbon skeletons has been the subject of a number of investigations.[3,4] The authors found that the epoxide I decomposed completely when subjected to gas–liquid chromatography through a column of Reoplex 400 (10% on acid-washed Chromosorb W). Infrared and n.m.r. examination proved the major degradation product (62%) to be an unsaturated aldehyde II with infrared absorption bands at 3080, 1632, and 885 cm.$^{-1}$ (>C=CH_2) and 2688 and 1726 cm.$^{-1}$ (—CHO) and n.m.r. peaks at 9.30 (—CHO), 4.40, and 4.61 p.p.m. (>C=CH_2) (tetramethylsilane = 0). Catalytic hydrogenation of the aldehyde ($C_{15}H_{24}O$) showed the presence of one double bond. Chromic acid oxidation of the saturated alcohol (III) obtained yielded the corresponding saturated aldehyde V having infrared absorption bands at 2698 and 1726 cm.$^{-1}$ and n.m.r. peak at 9.26 p.p.m. This aldehyde was also formed when subjecting dihydrocaryophyllene oxide (IV) to gas chromatography under the experimental conditions. The saturated aldehyde V was, in turn, converted *via* desulfurization of its thioketal with Raney nickel to the corresponding saturated hydrocarbon VI. Gas chromatographic and infrared characteristics of this hydrocarbon were different from those displayed by caryophyllane. These observations suggested that a rearrangement of the caryophyllane carbon framework had taken place. Quantitative analysis of the n.m.r. spectra of aldehydes II and V established the presence of three and four methyl groups, respectively. Since during the rearrangement reaction the number of

(1) Paper XXV: *J. Soc. Cosmetic Chemists*, in press.
(2) I. C. Nigam and L. Levi, *J. Org. Chem.*, **29**, 2803 (1964).
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(4) E. W. Warnhoff, *Can. J. Chem.*, **42**, 1664 (1964).

methyl groups of each epoxide molecule remained the same and an aldehyde group was generated, it was concluded that during gas chromatography the nine-membered ring of the caryophyllene skeleton undergoes contraction to an eight-membered ring. Figure 1 illustrates the rearrangement of the epoxides to 4,10,10-trimethyl-7-methylenebicyclo[6.2.0]decane-4-carboxaldehyde (II) and 4,7,10,10-tetramethylbicyclo-[6.2.0]decane-4-carboxaldehyde (V), and also shows the conversion of either aldehyde to the saturated hydrocarbon, 2,5,5,9,9-pentamethylbicyclo[6.2.0]decane (VI). Formulas shown in Figure 1 are also in agreement with Warnhoff's recent work.[4]

Rearrangement of the epoxides failed to take place when the support (acid-washed Chromosorb W) was treated with methanolic KOH,[5] and used under the experimental conditions described. In this case unchanged starting materials only were recovered. Evidently the transformation is triggered by active surfaces of the acidic column support.

The reactions observed are of considerable value for the examination of essential oils and related products. They were applied successfully by the authors for detecting the presence of caryophyllene oxide in oil of marihuana for the first time.[6]

Experimental

Gas chromatographic apparatus and procedures were previously described.[7] Infrared spectra were charted with a Perkin-Elmer Model 221 instrument. N.m.r. spectra were recorded in carbon tetrachloride solution, with a Varian A-60 spectrometer.

Caryophyllene Oxide (I).—The terpenoid was obtained by epoxidation (monoperphthalic acid) of pure caryophyllene (1.0 g.) isolated by preparative gas chromatography from oil of copaiba balsam. Recrystallization of crude product from methanol yielded pure substance (620 mg., m.p. 64°).

Rearrangement of Caryophyllene Oxide to 4,10,10-Trimethyl-7-methylenebicyclo[6.2.0]decane-4-carboxaldehyde.—Caryophyllene oxide (500 mg., in a few drops of benzene) was injected repeatedly into a gas chromatographic column packed with Reoplex 400 (10%) deposited on acid-washed Chromosorb W. (column temperature 200°, helium flow 75 ml./min.). Effluents corresponding to the major peak observed were collected in small tubes packed with glass wool and moistened with carbon tetrachloride. The aldehyde obtained (280 mg.) possessed the following characteristics: $n^{25}D$ 1.499, d^{20}_{20} 0.993, retention time 8.4 min.

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.75; H, 10.97. Found: C, 81.4; H, 11.2.

Dihydrocaryophyllene Oxide (IV).—Caryophyllene oxide (I) (101 mg.) was dissolved in 5 ml. of ethanol and hydrogenated in the presence of Adams catalyst (8 mg.) at room temperature and atmospheric pressure (hydrogen uptake 13.6 ml., yield of crude dihydrocaryophyllene oxide 95 mg.).

4,7,10,10-Tetramethylbicyclo[6.2.0]decane-4-carboxaldehyde.

A. From Aldehyde (II).—The conversion was carried out in two steps.

Hydrogenation to Alcohol III. A sample (200 mg.) was hydrogenated in ethanolic solution in the presence of Adams catalyst (25 mg.) (volume of hydrogen absorbed 40 ml.). The product of hydrogenation (192 mg.), recovered after usual processing, displayed strong hydroxyl absorption at 3390 cm.$^{-1}$. Retention time on Reoplex 400 (10%) was 10.9 min. (temperature 200°; helium flow 75 ml./min.).

Oxidation of Alcohol III.—The alcohol (180 mg.) was dissolved in pyridine (2 ml.) and allowed to react overnight with a solution of chromium trioxide (180 mg.) in pyridine (4 ml.). The reaction mixture was diluted with water and extracted with ether. The ether extract was treated with dilute sulfuric acid and, after washing with water, dried over sodium sulfate. The crude aldehyde (130 mg.) obtained following evaporation of solvent was chromatographed over 6.5 g. grade II alumina, using petroleum ether and benzene as eluents. The sample recovered from the benzene fraction and purified by gas chromatography exhibited a retention time of 7.8 min. on Reoplex 400 (10%) (column temperature 200°, helium flow 75 ml./min.).

B. From Dihydrocaryophyllene Oxide.—Small samples (15 μl.) of dihydrocaryophyllene oxide (IV) were passed through the Reoplex column at 200° and the major component was collected for analysis. Gas chromatographic and infrared characteristics of the product obtained were identical with those of the sample prepared in accordance with method A. Hydrogenation of the aldehyde yielded the saturated alcohol III, its identity being established by infrared and gas chromatographic analysis.

2,5,5,9,9-Pentamethylbicyclo[6.2.0]decane (VI).—Boron trifluoride etherate (50 μl.) was added slowly to an ice-cooled mixture containing the saturated aldehyde V (10 mg.) and ethanedithiol (45 μl.). Glacial acetic acid was added drop by drop until a homogeneous solution was obtained. The reaction mixture was kept at room temperature for 1 hr., poured into an aqueous solution of potassium carbonate, and extracted with ether. The ether extract was washed repeatedly with 10% sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated. The residue was refluxed with 2 ml. of a suspension of Raney nickel overnight, the catalyst was filtered off, and the filtrate was diluted with 10 ml. of water and extracted with petroleum ether. The extract was dried over anhydrous sodium sulfate and evaporated. The residue (9 mg.) was analyzed by gas chromatography. Retention time of hydrocarbon relative to caryophyllane was 0.69 (column 10% silicone nitrile XE-60, temperature 130°, helium flow 75 ml./min.).

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The Isolation of Palustric Acid from Gum Rosin

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Palustric acid, one of the major components of rosin, was first isolated by Loeblich, *et al.*,[2] and its structure was established by Schuller, *et al.*[3]

This acid represents about 10% of the acidic portion of pine gum and up to 18% of the acidic portion of gum rosin. It is a homoannular, conjugated-diene resin acid, λ^{alc}_{max} 265–266 mμ (ε 3300), $[\alpha]D$ +71.8°, and m.p. 162–167°.

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