

## TERPENOIDS—LIII\*

### STRUCTURE OF KHUSILAL, A NOVEL ALDEHYDE FROM VETIVER OIL

P. S. KALSI, K. K. CHAKRAVARTI and S. C. BHATTACHARYYA  
National Chemical Laboratory, Poona, India

(Received 23 June 1964)

**Abstract**—North Indian vetiver oil yielded a new laevorotatory aldehyde khusilal,  $C_{14}H_{18}O$ . Structure II has been assigned to it on the basis of UV, IR and NMR spectra and chemical evidence.

In previous communications<sup>1</sup>, the isolation and characterization of several hydrocarbons and alcohols from North Indian vetiver oil (*Vetiveria zizanioides*, Linn.) have been described. From the carbonyl fraction of the oil, a new highly laevorotatory liquid aldehyde,  $C_{14}H_{18}O$ ,  $[\alpha]_D^{25} -261^\circ$ , has now been isolated as the major constituent. We propose to name it as khusilal. It possesses a novel  $C_{14}$ -system which has not so far been encountered among terpenoids, though the  $C_{14}$ -ketone norketoagarofuran,<sup>2</sup>  $C_{14}H_{22}O_2$ , was isolated in this Laboratory from agarwood oil. An azulogenic lactone, mexicanin E,  $C_{14}H_{16}O_3$ , has also been reported.<sup>3</sup>

Evidence presented in this communication shows that khusilal has structure II. Direct chromatography of the carbonyl fraction of the vetiver oil over alumina was relatively ineffective for the separation of khusilal from other carbonyl components and resulted in considerable loss. However, the fraction yielded at low temperature copious amount of the semicarbazone of khusilal,  $C_{15}H_{21}ON_3$ , m.p.  $162^\circ$  ( $\lambda_{\max} 265$  m $\mu$ ,  $\epsilon 28,850$ ). On treatment with oxalic acid<sup>4</sup> this semicarbazone yielded the parent aldehyde khusilal as a pure (VPC), colourless, mobile liquid. The aldehyde regenerated from the semicarbazone could be reconverted to the same semicarbazone indicating that no change had taken place during these operations. The presence of an aldehyde group was confirmed by positive tests with Fehling's solution and ammoniacal silver nitrate. Khusilal readily yielded a deep red 2,4-dinitrophenylhydrazone,  $C_{20}H_{22}O_4N_4$ , m.p.  $214^\circ$  ( $\lambda_{\max}^{CHCl_3} 378$  m $\mu$ ,  $\epsilon 20,000$ ) and a white crystalline oxime,  $C_{14}H_{18}ON$ , m.p.  $101-102^\circ$  ( $\lambda_{\max} 235$  m $\mu$ ,  $\epsilon 18,270$ ).

The IR spectrum of khusilal (Fig. 1) showed bands at 2703 and 1678 typical of an  $\alpha,\beta$ -unsaturated aldehyde function; 3080, 1634 and 892 due to methylenic double bond ( $>C=CH_2$ ); 1818, 995 and 918 due to a vinyl double bond ( $—CH=CH_2$ ) and

\* Contribution No. 688 from the National Chemical Laboratory, Poona-8, India.

<sup>1</sup> P. S. Kalsi, K. K. Chakravarti and S. C. Bhattacharyya, *Tetrahedron* **18**, 1165 (1962); *ibid.* **19**, 1073 (1963); C. C. Kartha, P. S. Kalsi, A. M. Shaligram, K. K. Chakravarti and S. C. Bhattacharyya, *Tetrahedron* **19**, 241 (1963); A. A. Rao, K. L. Surve, K. K. Chakravarti and S. C. Bhattacharyya, *Tetrahedron* **19**, 233 (1963); A. M. Shaligram, A. S. Rao and S. C. Bhattacharyya, *Tetrahedron* **18**, 969 (1962).

<sup>2</sup> M. L. Maheshwari, K. R. Varma and S. C. Bhattacharyya, *Tetrahedron* **19**, 1519 (1963).

<sup>3</sup> A. Romo De Vivar and J. Romo, *J. Amer. Chem. Soc.* **83**, 2326 (1961); J. Romo, A. Romo De Vivar and W. Herz, *Tetrahedron* **19**, 2317 (1963).

<sup>4</sup> R. Howe and F. J. McQuillin, *J. Chem. Soc.* 2423 (1955).

840, 810 and 785  $\text{cm}^{-1}$  due to a trisubstituted ethylenic linkage ( $\text{CH}=\text{CR}_1\text{R}_2$ ). The UV absorption spectra of khusilal ( $\lambda_{\text{max}} 232 \text{ m}\mu$ ,  $\epsilon 12,320$ ) confirmed the presence of a conjugated enone chromopore.

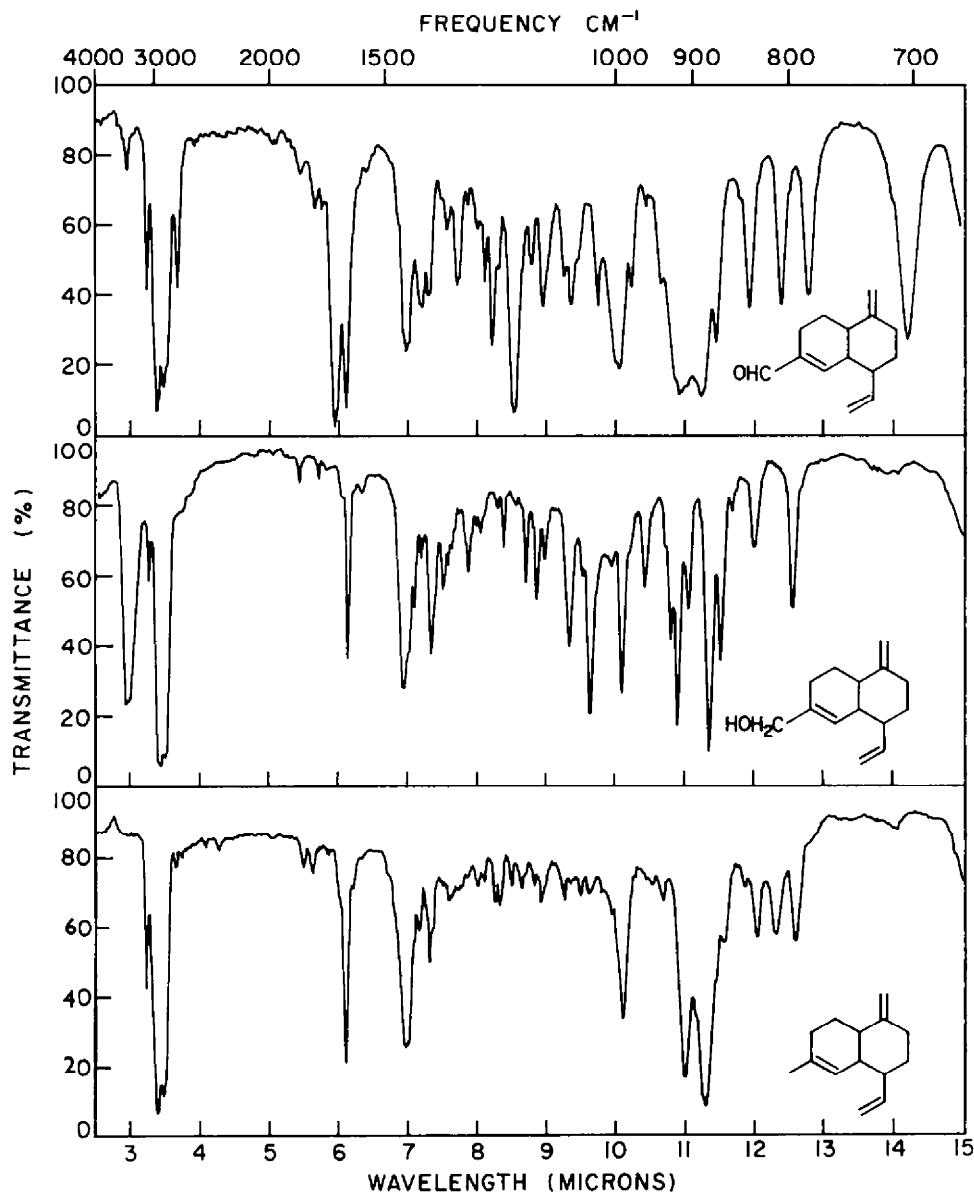
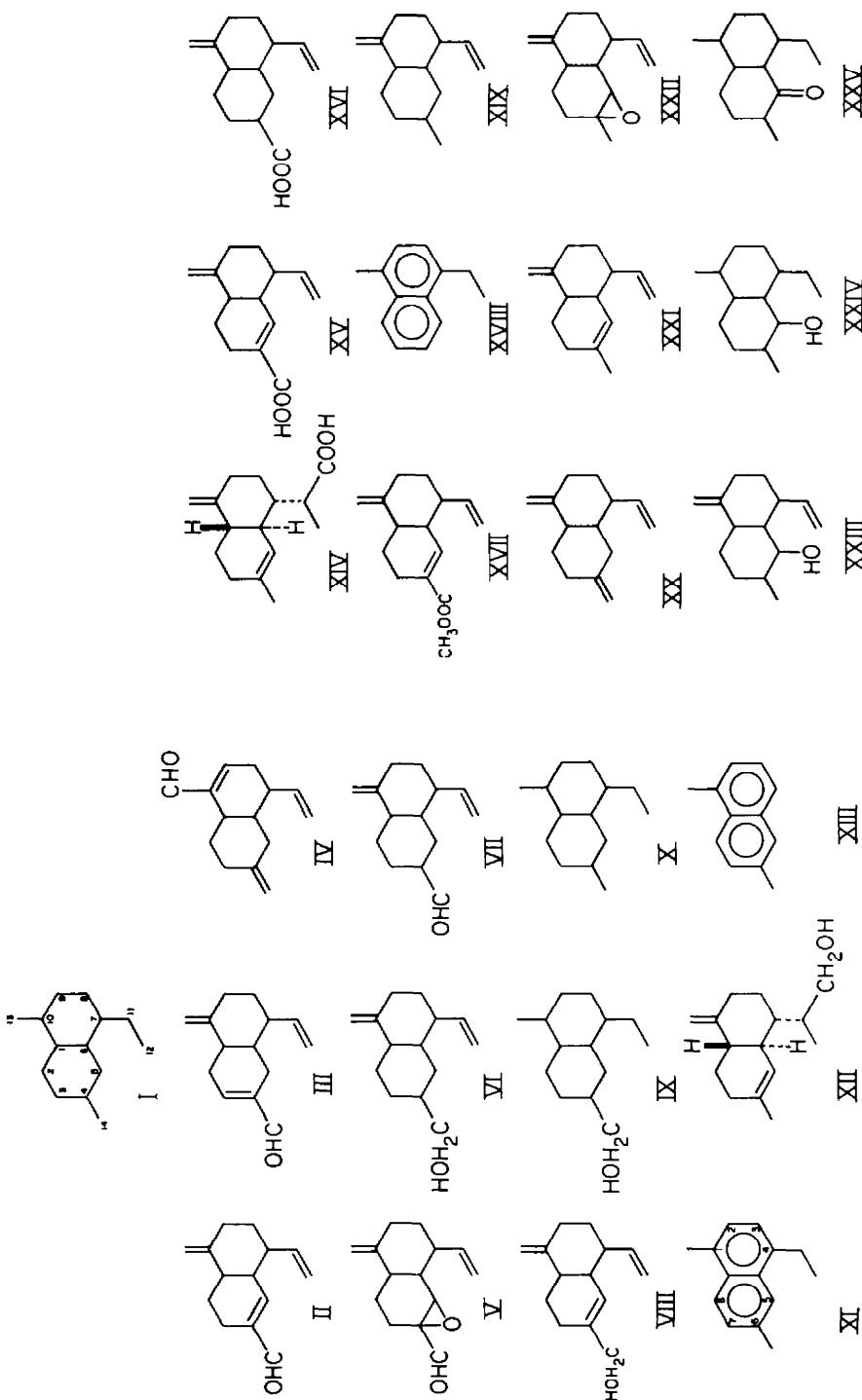


FIG. 1

Epoxy khusilal (V),  $\text{C}_{14}\text{H}_{16}\text{O}_2$ , was prepared by treatment of khusilal with alkaline hydrogen peroxide.<sup>5</sup> The IR spectrum ( $2703$  and  $1724 \text{ cm}^{-1}$ ) of the epoxy compound was characteristic of a saturated aldehyde function and lacked the characteristic UV absorption of a conjugated aldehyde. In its IR spectrum, the epoxy aldehyde showed

<sup>5</sup> P. L. Julian, E. W. Meyer, W. J. Karpel and I. R. Waller, *J. Amer. Chem. Soc.* **72**, 5145 (1950).



intense bands due to methylenic and vinyl double bonds while the bands ascribable to trisubstituted ethylenic linkage were absent. Thus the trisubstituted double bond is in conjugation with the aldehyde function. This fact was further confirmed by the reduction of khusilal to the crystalline alcohol dihydrokhusilol (VI),  $C_{14}H_{22}O$ , m.p.  $72^\circ$ ,  $[\alpha]_D^{24} - 30^\circ$  and the aldehyde dihydrokhusilal (VII),  $C_{14}H_{20}O$ , (IR bands at:  $2710$  and  $1724\text{ cm}^{-1}$ , corresponding acid (XVI),  $C_{14}H_{20}O_2$ , m.p.  $101^\circ$ ; 2,4-dinitrophenyl hydrazone,  $C_{20}H_{24}O_4N_4$ , m.p.  $174^\circ$ ) with sodium in aqueous ammonia.<sup>6</sup> In their IR

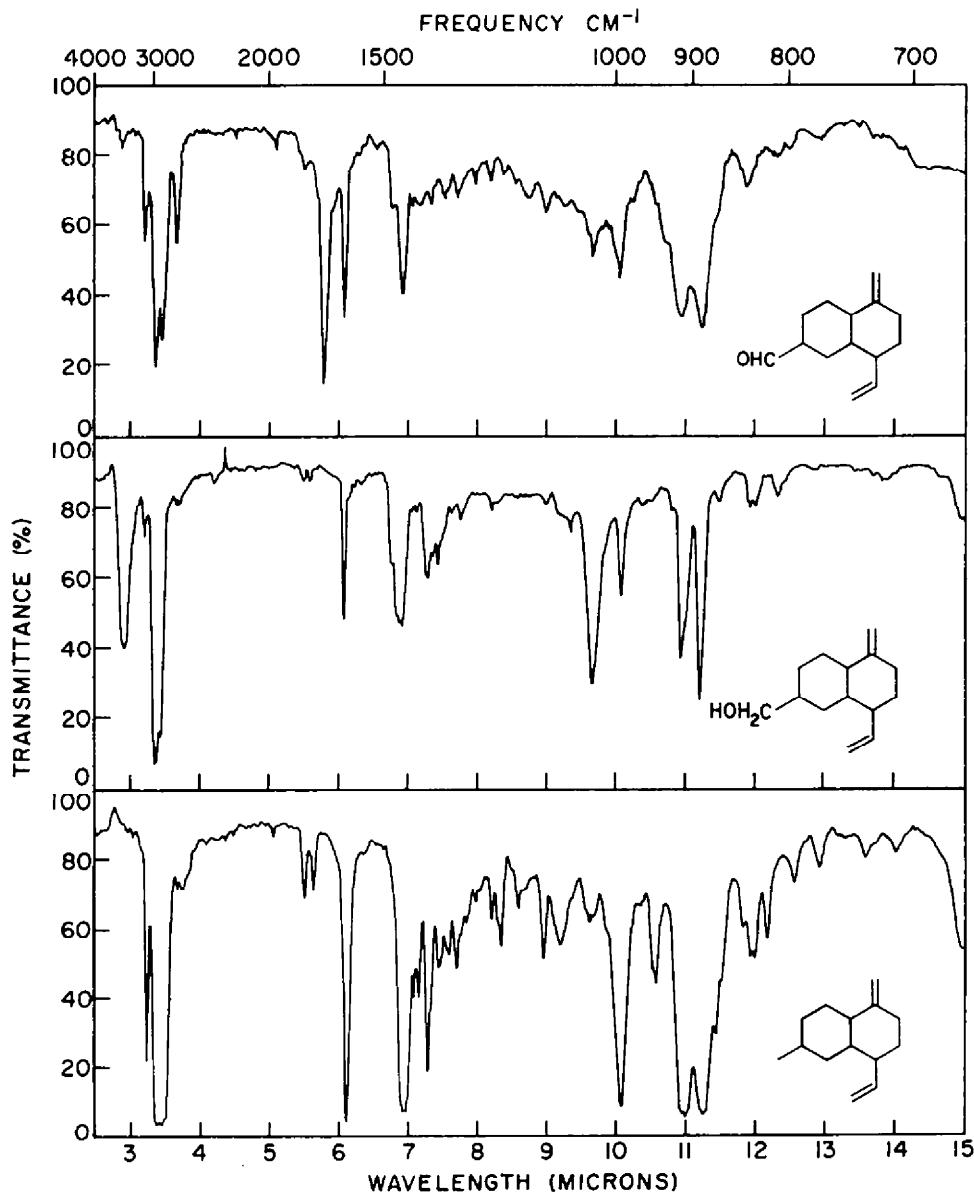


FIG. 2

<sup>6</sup> H. Ueda and S. Shimizu, *Bull. Arg. Chem. Soc. Japan* **23**, 524 (1959).

spectra (Fig. 2), dihydrokhusilal and dihydrokhusilol retained the bands due to methylenic and vinyl double bonds, the absorptions due to trisubstituted double bond being absent.

Reduction of khusilal with lithium aluminium hydride gives the corresponding alcohol khusilol (VIII),  $C_{14}H_{20}O$ , m.p.  $74^\circ$ ,  $[\alpha]_D^{24} - 158^\circ$ , IR spectrum (Fig. 1). Khusilol does not show any UV absorption maximum, indicating absence of conjugation among the double bonds in khusilal. Catalytic reduction of khusilol in acetic acid medium using Adams catalyst consumed 3.6 moles of hydrogen indicating the allylic position of the hydroxyl group to one of the three double bonds. In agreement with

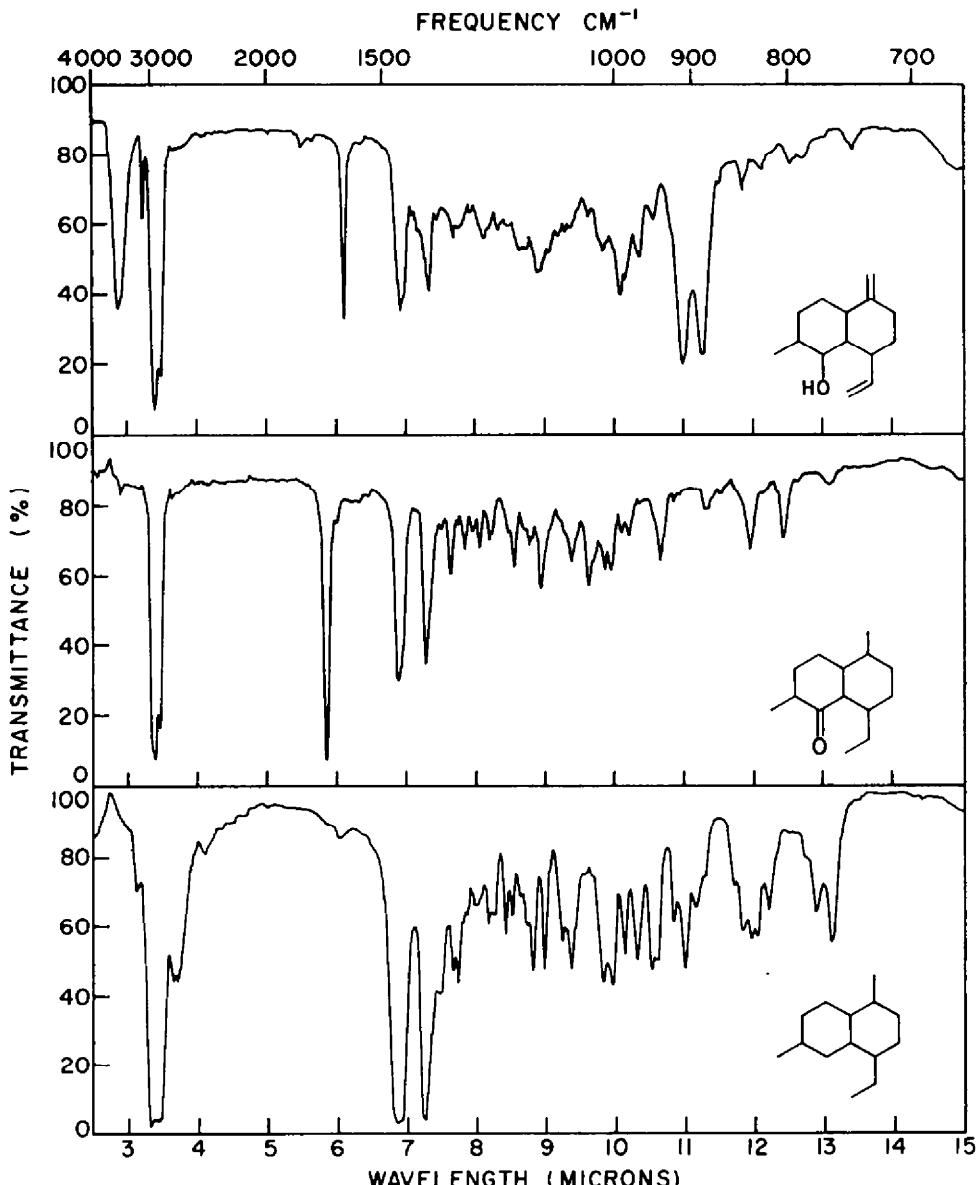


FIG. 3

this, the hydrogenation product gives a saturated hydrocarbon hexahydrokhusilene (X),  $C_{14}H_{26}$  (IR spectrum, Fig. 3), and a saturated alcohol hexahydrokhusilol (IX),  $C_{14}H_{26}O$ . Hydrogenation in alcoholic medium using Adams catalyst however absorbed only 3 moles hydrogen giving hexahydrokhusilol (IX), thus confirming the presence of 3 double bonds in khusilal. The alcohol (IX) does not show any end absorption around  $210\text{ m}\mu$  region indicating the absence of tetra-alkylated double bond, further supported by a negative tetranitromethane test. Neither khusilal nor khusilol shows the presence of methyl group on C-methyl determination.

Khusitol on dehydrogenation with selenium, gives 1,6-dimethyl-4-ethylnaphthalene (XI),  $C_{14}H_{16}$  (IR spectrum, Fig. 4), as the main product (90%, VPC) together

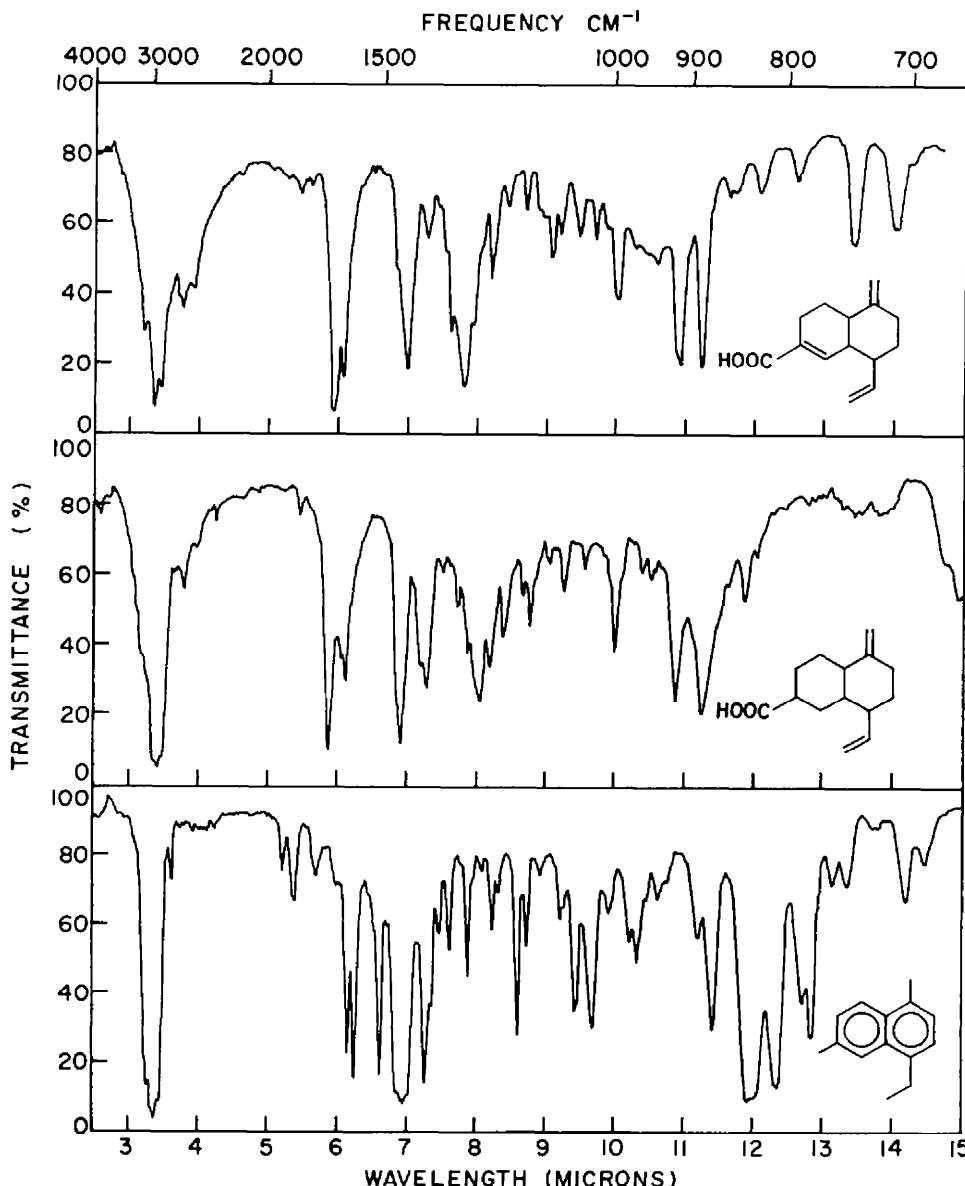


FIG. 4

with only a small amount of 1,6-dimethylnaphthalene (XIII). 1,6-Dimethyl-4-ethyl-naphthalene was identified by gas chromatography with an authentic sample prepared earlier from khusol<sup>1</sup> (XII) and by mixed m.p. of its TNB adduct with that of an authentic specimen. 1,6-Dimethyl-4-ethylnaphthalene is also obtained in high yields by the dehydrogenation of dihydrokhusilene (XIX),  $C_{14}H_{22}$ , prepared via dihydrokhusilol (VI) by tosylation and subsequent reduction with lithium aluminium hydride. This accounts for all the 14 carbon atoms of khusilal and consequently its basic skeleton should be represented by I. These results would suggest 3 possible structures (II, III and IV) for khusilal. The relative positions of the aldehydic carbonyl and exocyclic methylene in khusilal have been assigned on the basis of the formation of dehydrogenation products from its corresponding acid.

Oxidation of khusilal with alkaline silver oxide gives the corresponding crystalline  $\alpha, \beta$ -unsaturated acid (XV),  $C_{14}H_{18}O_2$ , m.p.  $124^\circ$  ( $\lambda_{\max} 215 \text{ m}\mu, \epsilon 9,482$ ) in low yields but this oxidation is not always reproducible. Similar observations have been made by other workers dealing with oxidation of  $\alpha, \beta$ -unsaturated aldehydes.<sup>7,8</sup> The acid (XV) is, however, obtained in high yields by oxidation of khusilal with chromic acid in acetone<sup>9</sup> and is identical (IR spectrum, Fig. 4) in all respects with the acid prepared by silver oxide oxidation of khusilal. The equivalent weight of the acid (XV) further confirmed the molecular formula of khusilal as  $C_{14}H_{18}O$ . Its methyl ester (XVII),  $C_{15}H_{20}O_2$ , ( $\lambda_{\max} 217 \text{ m}\mu, \epsilon 10,500$ ), on reduction with lithium aluminium hydride, is reconverted to the crystalline alcohol khusilol (VIII). The crystalline acid (XV) on dehydrogenation with selenium gives two main dehydrogenation products 1-methyl-4-ethylnaphthalene (XVIII) and 1,6-dimethyl-4-ethylnaphthalene (XI), in the ratio 3:2 (on the basis of VPC with authentic samples). During dehydrogenation of the acid the 6-methyl group in 1,6-dimethyl-4-ethylnaphthalene originated from the carboxyl group at that position.<sup>10-12</sup> The formation of 1-methyl-4-ethylnaphthalene (XVIII) shows that aldehyde group in khusilal is present at position 4 of structure (I), which eliminates structure IV for consideration.

We have also re-investigated the dehydrogenation of the acid (XIV), now prepared by an improved method<sup>9</sup> from khusol<sup>1</sup> (XII) with selenium. In addition to the already reported 1,6-dimethyl-4-ethylnaphthalene, 1,6-dimethylnaphthalene is also obtained in almost equal amounts (on the basis of VPC with authentic samples).

To prepare the parent hydrocarbon khusilene (XXI), khusilol (VIII) is tosylated at room temperature. It is interesting to note that after working up as usual neither the tosylate nor the starting alcohol could be isolated, but only water-soluble products were formed.\* The dihydrokhusilol (VI), however, can be converted to its corresponding tosyl derivative in quantitative yields which on reduction with lithium aluminium hydride gives the hydrocarbon dihydrokhusilene (XIX) in a pure form (VPC).

\* Similar behaviour has been observed with several other allylic primary alcohols in our laboratory.

<sup>7</sup> R. B. Woodward, F. Sndheimer, D. Taub, K. Heusler and W. M. McLamore, *J. Amer. Chem. Soc.* **74**, 4223 (1952).

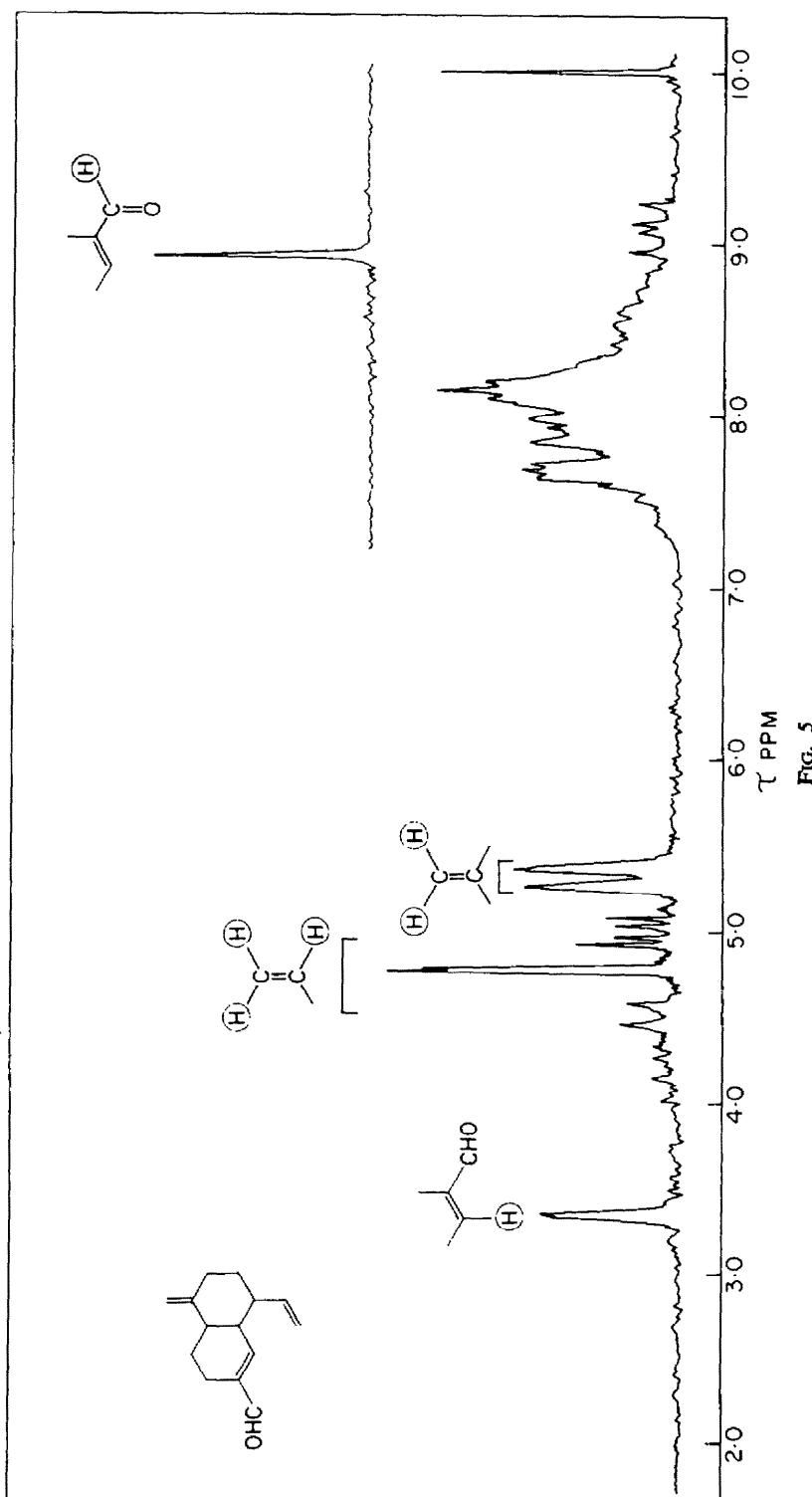
<sup>8</sup> L. B. Barkley, M. W. Farrar, S. Knowles and H. Raffelson, *J. Amer. Chem. Soc.* **76**, 5017 (1954); P. de Mayo, E. Y. Spencer and R. W. White, *Canad. J. Chem.* **39**, 1608 (1961); *J. Amer. Chem. Soc.* **84**, 494 (1962).

<sup>9</sup> K. Bowden, I. H. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.* **39** (1946).

<sup>10</sup> S. W. Pelletier, *Tetrahedron*, **14**, 76 (1961).

<sup>11</sup> W. A. Jacobs, *J. Org. Chem.* **16**, 1593 (1951).

<sup>12</sup> K. Wiesner, J. R. Armstrong, M. F. Bartlett and J. A. Edwards, *J. Amer. Chem. Soc.* **76**, 6068 (1954).



Subsequently, the semicarbazone of khusilal is subjected to Wolff-Kishner reduction to give the hydrocarbon XX with expected double bond shift,<sup>13-16</sup> confirmed by its IR and NMR spectra. Modified Wolff-Kishner reduction of the semicarbazone according to Grundon *et al.*<sup>15</sup> however gives the expected hydrocarbon khusilene (XXI),  $C_{14}H_{20}$  (IR spectrum, Fig. 1). To ascertain the position of the trisubstituted double bond in khusilal, khusilene is converted to its mono-epoxide (XXII) which on reduction with lithium aluminium hydride affords a secondary alcohol (XXIII),<sup>16</sup>  $C_{14}H_{22}O$  (IR spectrum, Fig. 3). Reduction of the latter with palladium-charcoal in ethanol gives the corresponding tetrahydro derivative (XXIV),  $C_{14}H_{23}O$ , which on oxidation furnishes the ketone (XXV),  $C_{14}H_{24}O$ . The IR spectrum of this ketone (Fig. 3) shows an intense band at  $1706\text{ cm}^{-1}$  for the carbonyl function on a six-membered ring, absorption in the vicinity of  $1420\text{ cm}^{-1}$  due to a  $-\text{CO}-\text{CH}_2-$  grouping being absent. This establishes the structure II for khusilal. The NMR spectrum of khusilal (Fig. 5) supports this structure.

## EXPERIMENTAL

All m.ps are uncorrected. Rotations were measured in  $\text{CHCl}_3$  solution. The alumina used for chromatography was acid-washed and activated and graded according to the Brockman scale of activity.<sup>17,18</sup> The pet. ether refers to the fraction boiling between  $60-80^\circ$ . The UV spectra were measured in ethanol solution unless otherwise stated on a Beckman ratio recording spectrophotometer, Model DK-2. The IR spectra were recorded as liquid film or in nujol suspension on a Perkin-Elmer infracord spectrophotometer, Model No. 137B. The NMR spectra were recorded with a Varian A-60 spectrometer operating at 60 mc, tetramethyl silane was added as an internal standard. Microanalyses were carried out in the Microanalytical Section of the laboratory.

### *Isolation of khusilal semicarbazone*

Vetiver oil (1 kg) obtained from Bharatpur in North India was chromatographed on alumina (grade III, 20 kg) and eluted successively with pet. ether (40 l.), benzene (45 l.) and ether (30 l.). The product (450 g) obtained by elution with pet. ether was further chromatographed on alumina (grade II, 30 kg) in the same manner and the carbonyl fraction (150 g) obtained by elution with benzene was rich in khusilal; IR bands at: 2710, 1680, 1709, 1725, 1637, 1000, 917, 892, 840 and  $790\text{ cm}^{-1}$ ; UV spectrum:  $\lambda_{\text{max}}$   $232\text{ m}\mu$ ,  $\epsilon$  5,100.

The carbonyl fraction (150 g) was mixed with ethanol (50 ml) and a solution of semicarbazide hydrochloride (60 g) and sodium acetate (90 g) in water (400 ml). The mixture was kept at  $0^\circ$  for 24 hr with occasional shaking. The semicarbazone was obtained in the form of a yellow cake which was washed repeatedly with ice-cold pet. ether when white solid (80 g) was obtained. On crystallization from dilute alcohol, long white needles were obtained, m.p.  $161^\circ$  (sample dried for 4 hr at  $95^\circ$  at 8 mm). (Found: N, 15.92.  $C_{14}H_{21}ON_3$  requires: N, 16.2%). UV spectrum:  $\lambda_{\text{max}}$   $265\text{ m}\mu$ ,  $\epsilon$  28,850.

### *Khusilal (II)*

Semicarbazone of khusilal (10 g) in ethanol (100 ml) and pet. ether (80 ml) was refluxed for 11 hr with oxalic acid (30 g) and 40% aq formaldehyde (50 ml). The pet. ether layer was separated and the aqueous layer was extracted several times with pet. ether. The combined ethereal extracts (200 ml) were washed with water till neutral, dried and the ether evaporated. The residue (5 g) was chromatographed over alumina (grade II, 100 g) and the column eluted with pet. ether (250 ml) to give khusilal (4.5 g), b.p.  $115^\circ$ (bath)/0.3 mm.  $n_D^{25}$  1.5349;  $[\alpha]_D^{25} -261^\circ$  (c, 9.7) (Found: C, 83.18; H, 9.04.  $C_{14}H_{18}O$  requires: C, 83.12; H, 8.97%); neutralization equivalent of its crystalline acid (XV),  $C_{14}H_{18}O_2$ ,

<sup>13</sup> Lardelli and Jeger, *Helv. Acta* 32, 1817 (1949).

<sup>14</sup> T. R. Ames, J. L. Beton, A. Bowers, T. G. Halsall and E. R. H. Jones, *J. Chem. Soc.* 1909 (1952).

<sup>15</sup> M. F. Grundon, H. B. Henbest and M. D. Scott, *J. Chem. Soc.* 1855 (1963).

<sup>16</sup> O. Motl, V. Sykora, V. Herout and F. Sorm, *Coll. Czech. Chem. Comm.* 23, 1297 (1958).

<sup>17</sup> H. Brockmann and H. Schodder, *Ber. Dtsch. Chem. Ges.* 74, 73 (1941).

<sup>18</sup> E. Lederer and M. Lederer, *Chromatography*, p. 26. Elsevier, N.Y. (1957).

219 (calc: 218.28). IR spectrum (Fig. 1) bands at: 2703, 1678, 3060, 1634, 892, 1818, 995, 918, 840, 810, 785 and 704  $\text{cm}^{-1}$ . UV spectrum:  $\lambda_{\text{max}}$  232  $\text{m}\mu$ ,  $\epsilon$  12,320. NMR spectrum (Fig. 5). Signals at: 0.6  $\tau$  (singlet) —  $\text{CH}=\text{C}-\text{CHO}$ , 3.38  $\tau$  (singlet) —  $\text{CH}=\text{C}-\text{CHO}$ , 4.5–4.9  $\tau$  (multiplet) —  $\text{CH}=\text{CH}_2$ , 5.25 and 5.35  $\tau$  (doublet)  $>\text{C}=\text{CH}_2$ .

#### *Oxime of khusilal*

Khusilal (1 g) was refluxed for 1/2 hr with a mixture of pyridine (1 ml), ethanol (12 ml, 95%) and hydroxylamine hydrochloride (0.5 g). It was crystallized from pet. ether to furnish white plates, m.p. 101–102° (Found: N, 6.73;  $\text{C}_{14}\text{H}_{19}\text{ON}$  requires: N, 6.45%). UV spectrum:  $\lambda_{\text{max}}$  235  $\text{m}\mu$ ,  $\epsilon$  18,270.

#### *2,4-Dinitrophenylhydrazone of khusilal*

To a hot solution of khusilal (II, 0.5 g) in ethanol (15 ml) a solution of 2,4-dinitrophenylhydrazine in ethanol–acetic acid mixture was added. The solution, after heating on a water bath for 10 min, was cooled and the derivative crystallized from ethanol– $\text{CHCl}_3$  mixture in the form of deep red leaflets, m.p. 214° (Found: N, 14.17.  $\text{C}_{20}\text{H}_{22}\text{O}_4\text{N}_4$  requires: N, 14.65%). UV spectrum:  $\lambda_{\text{max}}^{\text{CHCl}_3}$  378  $\text{m}\mu$ ,  $\epsilon$  20,000.

#### *Epoxy khusilal (V)*

To a solution of khusilal (1 g) in methanol (65 ml) at 0–5° was added a solution of 4N NaOH aq (2 ml) and  $\text{H}_2\text{O}_2$  (4 ml, 30%). The mixture was kept at 5° for 16 hr. The mixture was then poured into water (250 ml) and the epoxide isolated by  $\text{CHCl}_3$  extraction. The  $\text{CHCl}_3$  layer was washed repeatedly with water and dried. The solvent was evaporated and the product chromatographed over alumina (grade III, 30 g) and eluted with pet. ether: benzene (1:2) to yield the epoxide (0.6 g), b.p. 130°(bath/0.8 mm. (Found: C, 77.18; H, 8.66.  $\text{C}_{14}\text{H}_{18}\text{O}_2$  requires: C, 77.03; H, 8.31%). IR bands at: 3096, 2703(w), 1724, 1639, 990, 915, 890 and 842  $\text{cm}^{-1}$ ; no characteristic UV absorption.

#### *Dihydrokhusilol (VI) and dihydrokhusilal (VII)*

To a mixture of khusilal (8 g) in benzene (20 ml) and  $\text{NH}_4\text{OH}$  aq (20 ml, d 0.8) at –2° was added thin Na wire (7 g) in small portions with stirring. During the addition the temp was kept below 0° in the ice-salt bath. After the addition of half of the Na in 1 hr, additional amounts of benzene (15 ml) and  $\text{NH}_4\text{OH}$  aq (30 ml) were added. After all the Na had been added in 2 hr, stirring was continued for another 2 hr. The organic phase was extracted with ether (300 ml) and washed with cold dil. HCl (5%) and then with water till free from acid. It was dried and on evaporation of the solvent, the product (8 g) was isolated. It was chromatographed over alumina (grade II, 320 g).

(i) Elution of the column with pet. ether–benzene (1:1, 300 ml) gave (1 g) VII, b.p. 110°(bath/0.5 mm. (Found: C, 82.24; H, 9.47.  $\text{C}_{14}\text{H}_{20}\text{O}$  requires: C, 82.30; H, 9.87%). IR spectrum (Fig. 2) bands at: 3095, 2710, 1724, 1642, 998, 915 and 892  $\text{cm}^{-1}$ ; no UV absorption.

#### *2,4-Dinitrophenylhydrazone of dihydrokhusilal*

It was crystallized from ethanol– $\text{CHCl}_3$  mixture in the form of deep yellow leaflets, m.p. 174° (Found: N, 14.50.  $\text{C}_{20}\text{H}_{24}\text{O}_4\text{N}_4$  requires: N, 14.58%).

#### *Acid (XVI)*

It was prepared by the oxidation of dihydrokhusilal with chromic acid in acetone,<sup>9</sup> crystallized from pet. ether, m.p. 101° (Found: C, 76.47; H, 9.20.  $\text{C}_{14}\text{H}_{20}\text{O}_4$  requires: C, 76.32; H, 9.15%). IR spectrum in nujol (Fig. 4) bands at: 3077, 1706, 1639, 1000, 917 and 892  $\text{cm}^{-1}$ .

(ii) Elution with ether (400 ml) gave dihydrokhusilol (VI), (6.5 g), b.p. 132°(bath/0.25 mm.,  $n_D^{20}$  1.5180,  $[\alpha]_D^{20}$  –30° (c, 1.3) (Found: C, 81.72; H, 10.73.  $\text{C}_{14}\text{H}_{22}\text{O}$  requires: C, 81.50; H, 10.75%). This fraction solidified on standing at room temp and was crystallized from pet. ether to yield white silky needles, m.p. 72°. IR spectrum in nujol (Fig. 2) bands at: 3400, 3088, 1639, 1031, 990, 910 and 890  $\text{cm}^{-1}$ .

#### *Khusilol (VIII)*

A solution of khusilal (5 g) in dry ether (50 ml) was added dropwise to a stirred suspension of  $\text{LiAlH}_4$  (1.5 g) in dry ether (500 ml). The mixture was stirred at room temp for 10 hr under reflux and then the excess of reagent was decomposed by addition of water (30 ml) followed by cold dil.

HCl. After extraction with ether the product crystallized from pet. ether as long, white, silky needles (4.8 g), m.p. 75°,  $[\alpha]_D^{25} - 158^\circ$  (c, 2) (Found: C, 82.45; H, 9.97.  $C_{14}H_{20}O$  requires: C, 82.30; H, 9.87%).

IR spectrum in nujol (Fig. 1) bands at: 3400, 3088, 1639, 1042, 990, 917, 885, 833, and 795  $\text{cm}^{-1}$ .

No characteristic UV absorption. NMR spectrum signals at: 4.32  $\tau$  (singlet)  $-\text{HC}=\text{C}(\text{CH}_2\text{OH})-\text{CH}_2-$ , 4.5-5  $\tau$  (multiplet)  $-\text{CH}=\text{CH}_2$ , 5.4 and 5.48  $\tau$  (doublet)  $>\text{C}=\text{CH}_2$ , 6.02  $\tau$  (singlet)  $-\text{CH}=\text{C}(\text{H}_2\text{OH})-\text{CH}_2-$ , 8.36  $\tau$  (singlet)  $-\text{CH}=\text{C}(\text{CH}_2\text{OH})-$ .

#### *Hexahydrokhusilol (IX) and hexahydrokhusilene (X)*

(i) A solution of VIII (1.1 g) in acetic acid (50 ml) was hydrogenated in presence of prereduced Adams catalyst (140 mg).  $\text{H}_2$  absorbed (512 ml at 31° and 716 mm, 18 hr) corresponded to 3.6 moles. The catalyst was filtered off and the acetic acid removed *in vacuo* on a steam bath. The residue was chromatographed over alumina (grade II, 40 g) and eluted with pet. ether (150 ml) to yield X (0.59 g), b.p. 103°(bath)/3 mm,  $[\alpha]_D^{20} + 44^\circ$  (c, 3),  $n_D^{20}$  1.4761. (Found: C, 86.2; H, 13.8.  $C_{14}H_{20}$  requires: C, 86.51; H, 13.49%). IR spectrum in liquid cell 0.1 mm (Fig. 3). NMR spectrum signals at: 9.01, 9.11 and 9.2  $\tau$  (overlapping) two  $-\text{CH}=\text{CH}_2$  groups and one  $-\text{CH}_2=\text{CH}_2$  group. Ether eluted IX (0.38 g), b.p. 130°(bath)/0.9 mm,  $[\alpha]_D^{20} + 44^\circ$  (c, 1.4),  $n_D^{20}$  1.4965. (Found: C, 80.09; H, 12.41.  $C_{14}H_{20}O$  requires: C, 79.93; H, 12.46%). UV spectrum: no end absorption around 210  $\text{m}\mu$ ; no coloration with tetraniromethane.

(ii) A solution of VIII (0.6 g) in ethanol (20 ml) was hydrogenated in the presence of Adams catalyst (10 mg). The  $\text{H}_2$  absorbed (231 ml at 24° and 712 mm, 16 hr) corresponded to 3 moles. The product (0.55 g) was identical with IX.

#### *Dehydrogenation of khusilol (VIII) with Se*

Khusilol (0.4 g) was mixed with Se (0.8 g) and heated in  $\text{N}_2$  atm at 290° for 18 hr. The product in pet. ether was chromatographed over alumina (grade I, 20 g). The pet. ether eluate (0.23 g) on VPC analysis showed the presence of 1,6-dimethyl-4-ethylnaphthalene (XI) to the extent of 90% with small amounts of 1,6-dimethylnaphthalene (XII). The compound XI was isolated from the mixture in a pure form via its TNB derivative, m.p. 135° undepressed on admixture with an authentic specimen (Found: N, 10.63.  $C_{20}H_{18}O_2N_2$  requires: N, 10.58%). An analytical sample of XI had b.p. 128° (bath)/2 mm. (Found: C, 91.33; H, 8.63.  $C_{14}H_{16}$  requires: C, 91.25; H, 8.75%). IR spectrum in liquid cell 0.05 mm (Fig. 4).

#### NMR spectrum:

Signals at	Multiplicity	No. of protons	Assignment
2.13	doublet	one	$\text{H}_8$
2.21	singlet	one	$\text{H}_5$
2.74	doublet-doublet	one	$\text{H}_7$
2.89	singlet	two	$\text{H}_2$ & $\text{H}_3$
6.99	quadruplet	two	$\text{Ar}-\text{CH}_2-$
7.4	singlet	three	1— $\text{CH}_3$
7.48	singlet	three	6— $\text{CH}_3$
8.67	singlet	three	4— $\text{CH}_2-\text{CH}_3$

#### *Acid (XV) from Khusilal (II)*

(i) *Oxidation with alkali silver oxide.* To a cold solution of II (0.6 g) and powdered  $\text{AgNO}_3$  (1.2 g) in ethanol was added dropwise a solution of  $\text{NaOH}$  (0.8 g) in aq ethanol (20 ml) with stirring. After 24 hr at room temp (27°) the mixture was diluted with water and acidified with cold dil. HCl. It was extracted with ether and the ethereal solution washed with cold water and dried. After removal of the solvent, the acid XV (0.10 g), crystallized from pet. ether, m.p. 124°  $[\alpha]_D^{24} - 198^\circ$  (c, 2) (Found: C, 77.11; H, 8.55; eq. wt 219.  $C_{14}H_{14}O_4$  requires: C, 77.03; H, 8.31%; eq. wt 218.28). IR spectrum

in nujol (Fig. 4) bands at: 3077, 1675, 1639, 998, 910, 892, 830 and 791  $\text{cm}^{-1}$ ; UV spectrum:  $\lambda_{\text{max}}$  215  $\text{m}\mu$ ,  $\epsilon$  9,482.

(ii) *Oxidation with chromic acid in acetone.* The chromic acid solution (ca. 8N) used as the oxidizing agent was prepared by dissolving pure  $\text{CrO}_3$  (66.7 g) in water, adding conc.  $\text{H}_2\text{SO}_4$  (53.3 ml) and diluting the mixture with water to 250 ml. To a solution of II (6 g) in dry acetone (400 ml), chromic acid solution was added dropwise at room temp (26°) in 8 hrs till the solution retained the reddish colour of the oxidizing reagent. The mixture was diluted with water (300 ml) and the reaction product isolated with ether. The solvent was evaporated and the product (5.8 g) treated with saturated  $\text{Na}_2\text{CO}_3$  aq. It was extracted with ether (250 ml) to remove unreacted II (1.2 g). The  $\text{Na}_2\text{CO}_3$  solution was acidified with cold dil. HCl. It was extracted with ether and the ethereal solution washed repeatedly with cold water and dried. After removal of the solvent, the acid XV (4.2 g) crystallized from pet. ether, m.p. 124°,  $[\alpha]_D^{25}$  -200° (c, 1.2). The mixed m.p. with the sample prepared by  $\text{Ag}_2\text{O}$  oxidation of II remained undepressed and their IR and UV spectra were identical.

#### *Methyl ester of acid (XV)*

The acid (0.47 g) in dry ether was converted to its methyl ester (diazomethane) and chromatographed over alumina (grade II, 30 g) and eluted with pet. ether:benzene mixture (1:1) and distilled b.p. 130°(bath)/0.5 mm. (Found: C, 78.00; H, 8.86.  $\text{C}_{16}\text{H}_{20}\text{O}_3$  requires: C, 77.55; H, 8.68%). IR bands at: 3077, 1698, 1639, 1248, 990, 917, 892, 826 and 800  $\text{cm}^{-1}$ ; UV spectrum:  $\lambda_{\text{max}}$  217  $\text{m}\mu$ ,  $\epsilon$  10,500.

Reduction of the methyl ester with  $\text{LiAlH}_4$  gave the crystalline khusilol (VIII), m.p. and mixed m.p. 75°.

#### *Dehydrogenation of the acid (XV) with Se*

The crystalline acid (2 g) was mixed with Se (5 g) and heated in  $\text{N}_2$  atm. at 300° for 17 hr. The reaction mixture in pet. ether was filtered through alumina (grade I, 50 g). The product (0.7 g) on VPC analysis essentially showed the presence of two products, 1-methyl-4-ethylnaphthalene (XVIII) and 1,6-dimethyl-4-ethylnaphthalene (XI) in the ratio 3:2.

#### *Acid (XIV) from khusol (XII)*

To a solution of XII (3.4 g) in dry acetone (250 ml), chromic acid solution<sup>9</sup> was added dropwise at room temp (28°) till the solution retained the reddish colour of the oxidizing reagent (15 min). After working up in the customary manner the acid XIV (3.1 g) was crystallized from pet. ether, m.p. 119°;  $[\alpha]_D^{25}$  -120° (c, 2); mixed m.p. with an authentic sample prepared earlier<sup>1</sup> remained undepressed (Eq.wt. 234;  $\text{C}_{16}\text{H}_{22}\text{O}_2$  requires 234.33).

#### *Tosylation of dihydrokhusilol (VI)*

A mixture of dihydrokhusilol (5 g) in dry pyridine (30 ml) and freshly crystallized *p*-toluenesulphonyl chloride (6.5 g) in dry pyridine (60 ml) was kept at room temp (25°) for 50 hr. It was poured into crushed ice, taken up in ether and the ether layer washed successively with cold, dil. HCl,  $\text{NaHCO}_3$  aq and finally with water and dried. After the removal of the solvent the tosylate (6.4 g) was isolated. The IR spectrum showed absence of absorption in the vicinity of (3400  $\text{cm}^{-1}$ ) and showed intense bands due to tosyl group (1600, 1485, 1176 and 1100  $\text{cm}^{-1}$ ).

#### *Dihydrokhusilene (XIX)*

The tosyl derivative (5 g) in dry ether (20 ml) was added dropwise in 1 hr to a slurry of powdered  $\text{LiAlH}_4$  (2 g) in dry ether (20 ml) at 0° with stirring. The contents were then refluxed for 18 hr, the mixture decomposed with water (20 ml) and worked up to afford dihydrokhusilene (2.4 g) which was chromatographed over alumina (grade I, 100 g) and distilled over Na, b.p. 100°(bath)/0.8 mm,  $[\alpha]_D^{25}$  -22° (c, 2),  $n_D^{20}$  1.4980 (Found: C, 87.80; H, 11.90.  $\text{C}_{14}\text{H}_{22}$  requires: C, 88.35; H, 11.65%); single peak in VPC; IR spectrum in liquid cell 0.05 mm (Fig. 2) bands at: 3085, 1820, 1642, 995, 910 and 892  $\text{cm}^{-1}$ . NMR spectrum: signals ats 4.25 to 5.3  $\tau$  (multiplet)  $\text{--CH}=\text{CH}_2$ , 5.45 and 5.52  $\tau$  (doublet)  $\text{>C=CH}_2$ , 9.07  $\tau$  (doublet,  $J$  = 17 c/s)  $\text{--CH=CH}_3$ .

#### *Hydrocarbon (XX) by Wolff-Kishner reduction of the semicarbazone of khusilal (II)*

A mixture of the semicarbazone (1.7 g) diethylene glycol (30 ml) and KOH pellets (2 g) was heated at 110° for 2 hr in an atm. of  $\text{N}_2$ . Water from the reaction mixture was removed by raising the temp

gradually to 195° and then heating continued at 200° for 5 hr. The reaction product was diluted with water (100 ml), neutralized with cold dil. HCl and extracted with ether. The extract was made neutral, dried and evaporated. The product (1.5 g) was chromatographed over alumina (grade I, 50 g) giving the hydrocarbon XX (0.4 g) contaminated with slight aromatic impurities (UV spectrum:  $\lambda_{\text{max}}$  246, 252, 257, 263 m $\mu$ ;  $\epsilon$  650, 900, 850, 600). It was rechromatographed over alumina (grade I, 70 g), eluted with pet. ether and 6  $\times$  20 ml fractions were collected. Considering the UV spectra and VPC analysis fractions 2 to 4 were essentially pure. These were combined (0.21 g) and constituted the hydrocarbon (XX), b.p. 120°(bath)/4 mm,  $[\alpha]_D^{25} - 84^\circ$  (c, 1.1),  $n_D^{25}$  1.5140. (Found: C, 89.5; H, 10.8.  $C_{14}H_{20}$  requires: C, 89.29; H, 10.7%). IR spectrum bands at: 3085, 1639, 998, 910 and 892 cm $^{-1}$ . NMR spectrum signals at: 4.17 to 5.32  $\tau$  (multiplet) —CH=CH<sub>2</sub>, 5.48  $\tau$  (singlet) two >C=CH<sub>2</sub> groups.

#### *Khusilene (XXI) by modified Wolff-Kishner procedure*

A mixture of khusilal semicarbazone (10 g), toluene (250 ml) and potassium t-butoxide (5 g) was heated under reflux for 50 hr. After usual decomposition with water, the toluene layer was separated and the aqueous layer was extracted several times with ether. The combined ether and toluene solutions were washed several times with water and dried. Removal of the solvent gave a brown liquid (9 g). It was filtered through alumina (grade I, 450 g) and eluted with pet. ether (500 ml). The hydrocarbon XXI (5 g) was obtained in a state of 90% purity on the basis of VPC analysis. The IR spectrum showed the presence of aromatic impurities. It was chromatographed over alumina (grade I, 500 g) and 5  $\times$  100 ml pet. ether fractions were collected. Considering the spectroscopic data together with VPC analysis, fractions 4 and 5 consisted of almost pure khusilene (1.8 g), b.p. 100°(bath)/0.6 mm,  $[\alpha]_D^{25} - 102^\circ$  (c, 2.4),  $n_D^{25}$  1.5110. (Found: C, 89.30; H, 10.9.  $C_{14}H_{20}$  requires: C, 89.29; H, 10.71%). IR spectrum (Fig. 1) bands at: 3085, 1820, 1642, 998, 910, 892, 833, 815 and 795 cm $^{-1}$ . NMR spectrum signals at: 4.17 to 5.25  $\tau$  (multiplet) —CH=CR<sub>1</sub>R<sub>2</sub> and —CH=CH<sub>2</sub>;

5.4 and 5.48  $\tau$  (doublet) >C=CH<sub>2</sub>, 8.36  $\tau$  (singlet) >C=C—CH<sub>3</sub>.

#### *Alcohol (XXIII)*

Fractions 1-3 from the above experiment gave hydrocarbon (2.6 g) which was treated in CHCl<sub>3</sub> solution (150 ml) with perbenzoic acid in CHCl<sub>3</sub> (30 ml, 0.8108N) at 0° for 16 hr. The CHCl<sub>3</sub> solution was washed with NaHCO<sub>3</sub> aq, water and dried. Evaporation of the solvent gave crude epoxide XXII (2.5 g). The ethereal solution of XXII (10 ml) was added dropwise to a well dispersed suspension of LiAlH<sub>4</sub> (1.5 g) in ether (30 ml) and the reaction mixture was refluxed for 10 hr. The reaction mixture after working up gave the crude product (2.35 g) which was chromatographed over alumina (grade II, 60 g) and eluted with pet. ether (500 ml) to yield the unreacted hydrocarbon (0.49 g). The alcohol XXIII (1.5 g) was obtained by eluting the column with ether (400 ml), b.p. 125°(bath)/0.6 mm,  $[\alpha]_D^{25} - 17^\circ$  (c, 3) (Found: C, 81.14; H, 10.7.  $C_{14}H_{22}O$  requires: C, 81.50; H, 10.75%). IR spectrum (Fig. 3) bands at: 3400, 3080, 1820, 1634, 990, 909 and 887 cm $^{-1}$ .

#### *Ketone (XXV)*

The alcohol XXIII (1.6 g) was hydrogenated in the presence of Pd-C (1 g, 5%) in ethanol (30 ml) at 24° and 713 mm, the absorption of 1.9 moles H<sub>2</sub> was complete in 4 hr. The product (1.5 g) was purified by chromatography over alumina (grade II, 50 g) and eluting the column with benzene-ether (1:2, 500 ml) to yield the alcohol XXIV (1.39 g), b.p. 120°(bath)/0.6 mm. (Found: C, 79.50; H, 12.30.  $C_{14}H_{26}O$  requires: C, 79.93; H, 12.46%).

The alcohol XXIV (1 g) in acetone (150 ml) was treated with chromic acid solution in acetone<sup>10</sup> (6 ml). The reaction mixture was allowed to stand at room temp for 1/2 hr. After working up in the customary manner, the product was chromatographed over alumina (grade III, 30 g) and eluted with pet. ether to give the ketone XXV (0.49 g), b.p. 115°(bath)/0.5 mm,  $[\alpha]_D^{25} + 39^\circ$  (c, 1) (Found: C, 80.31; H, 11.77.  $C_{14}H_{24}O$  requires: C, 80.71; H, 11.61%). IR spectrum (Fig. 3) band at: 1706 cm $^{-1}$ .