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TERPENOIDS—LXXXI

TRANSFORMATION PRODUCTS OF ELEMOL AND EUDESMOL AND SYNTHESIS OF ELEMANONES AND SELINANONES*

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Abstract—Tetrahydroelemol and dihydroeudesmol undergo dehydration on treatment with traces of perchloric acid in acetic acid. The resulting hydrocarbons when subjected to (i) epoxidation followed by BF_3-etherate treatment, (ii) hydroboration-oxdiation followed by further oxidation with Jones chromic acid reagent give elemanones and selinanones respectively. From the reaction mixtures (−) elemane-8-one (VIII) and (−) selinane-8-one (XXIII) can be separated in pure states via their semicarbazones. (±) Elemane-8-one can be obtained by hydrogenation of pyrogermacrone. The hindered ketones elemane-6-one (VII) and selinane-6-one (XXII) or their corresponding alcohols could not be obtained in the pure state. Stereochemistry of the various products have been discussed and their ORD curves examined.

During the course of work on the dehydration of elemol (I) with perchloric–acetic acids, Paknikar and Bhattacharyya[1] observed that the double bond formed as a result of dehydration of the tertiary hydroxyl group migrated inside the ring. Following the same procedure we have now treated tetrahydroelemol (II). IR evidence indicates the absence of a methylenic double bond and shows the presence of a trisubstituted double bond which is also supported by the NMR spectrum and the absence of acetone and formaldehyde on ozonolysis. TLC and GLC analysis indicate the presence of two components, presumably III and IV in the ratio of 80 : 20. The epoxides (V and VI) obtained by perbenzoic acid oxidation of this hydrocarbon mixture on treatment with BF_3-etherate give a mixture of two ketones (VII and VIII). The ketone VII is inert and is separated from VIII via the semicarbazone of the latter and also by treatment with Girard's reagent. Ketone VII has been previously obtained by an independent method[2] from tetrahydrosaussurea lactone (IX) of known stereochemistry, thereby establishing the stereochemistry of the ketone from X. The ketone obtained from tetrahydrosaussurealactone has higher specific rotation (+60·84°). It also shows sharp characteristic NMR spectra, fully agreeing with the structure X. Ketone VII obtained via rearrangement of epoxide, as such, appears to be homogeneous by TLC and GLC analysis. There is little doubt that it is structurally identical with X. It, however, shows lower optical rotation (+36·34°). Its NMR spectrum, also somewhat different, suggests an epimeric mixture; epimerization having taken place during BF_3-treatment. It is possible that epimerization has affected either centre 5 or 7 or both, adjacent to the carbonyl group.† Ketone VIII was however obtained in the pure form by decomposition

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† This is also supported by comparative ORD measurements for which we are indebted to Prof. Klyne.

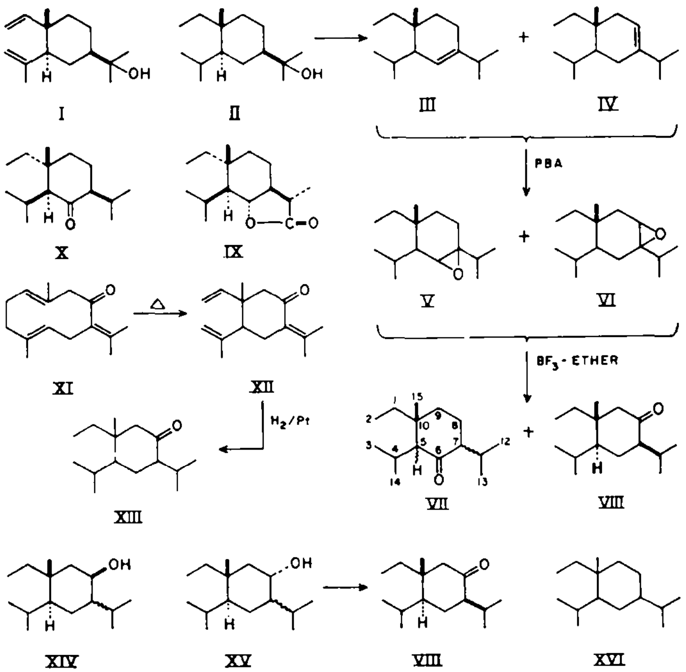
[1] S. K. Paknikar and S. C. Bhattacharyya, *Tetrahedron* **18**, 1509 (1962).

[2] A. D. Wagh, S. K. Paknikar and S. C. Bhattacharyya, *Tetrahedron* **20**, 2647 (1964).

of its constant melting (172–173°) semicarbazone. It is structurally identical with (±) hexahydropyrogermacrone[3] (β-elemanone[4]; XIII). The identity was proved by preparation of the authentic (±) sample from germacrone* (XI) and comparing the IR spectra of the parent ketone and also the mixed m.p. with the corresponding semicarbazones.

To avoid the complication arising, possibly out of BF_3-etherate treatment, the mixture of the hydrocarbons III and IV was subjected to hydroboration–oxidation. From this reaction, only the epimeric mixture of the alcohols XIV and XV were isolated and which on subsequent oxidation gave a ketone identical in all respects with VIII, obtained previously by the transformation of epoxides. In the case of VIII, because of the bulky nature of the isopropyl group, α to the carbonyl function, it should be only equatorially oriented.† A small amount of a saturated hydrocarbon, identified as elemane (XVI) was obtained as a byproduct during hydroboration–oxidation. These results also directly support that the methyl group at C_{10} and hydrogen at C_5 are *trans* oriented in elemanone (XIII; obtained from germacrone) and the isopropyl group β-oriented.

Chart I



Subsequently, the reactions mentioned were applied to dihydroeudesmol (XVII). The resulting hydrocarbon mixture (XVIII and XIX), on epoxidation and subsequent BF_3-treatment gave a mixture of ketones XXII and XXIII, which were separated by

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* We thank Prof. F. Sorm for the supply of a generous sample of germacrone.

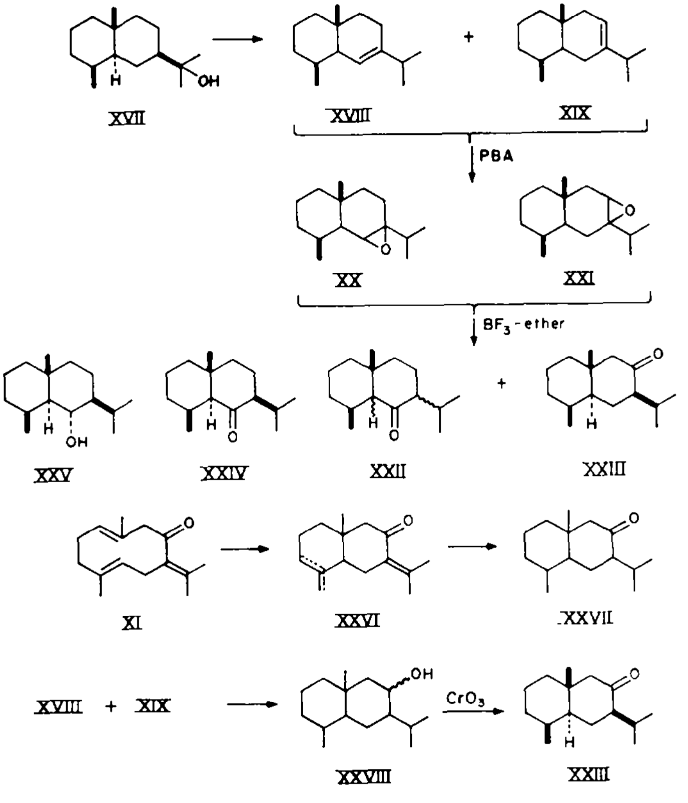
† Supported by ORD measurements carried out by Prof. Klyne.

[3] G. Ohloff, *Liebigs Ann.* **625**, 206 (1954).

[4] I. Ognjanov, V. Herout, M. Hoval and F. Sorm, *Coll. Czech. Chem. Comm.* **24**, 2371 (1959).

formation of the semicarbazone (m.p. 197–198°) of XXIII and also by treatment with Girard's reagent. The inert ketonic component (XXII) which is structurally identical with dihydrojunenone[5] (XXIV) was analytically pure but epimerically not homogeneous, as it gave on GLC four peaks, the major one constituting about 40% of the product being dihyrdojunenone as shown by comparative GLC analysis. Attempts to obtain pure dihydrojunenol (XXV) from it has not been successful. The ketone XXIII regenerated from its semicarbazone (m.p. 197–198°) was, however, pure by GLC and TLC analysis. It is structurally identical with (±) selinanone (XXVII) obtained previously by acid cyclization of germacrone followed by hydrogenation-oxidation.[6] The hydrocarbon mixture (XVIII and XIX) when subjected to hydroboration-oxidation gave a mixture of alcohols which was passed through grade III alumina and eluted with light petroleum-benzene (1:2). This eluate after removal of the solvent was again passed through silicic acid and eluted with benzene in 25 fractions. The first five fractions contained as many as four compounds as revealed by TLC and GLC analysis; one of these corresponded to dihydrojunenol. Attempts to separate it in pure form however were not successful. The later fractions of chromatography

CHART-2



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[5] V. Herout, O. Motl and F. Sorm, *Coll. Czech. Chem. Comm.* **22**, 785 (1957); S. C. Bhattacharyya, A. S. Rao and A. M. Shaligram, *Chem. & Ind.* 469 (1960); D. W. Theobald, *Tetrahedron* **20**, 2593 (1964).

[6] I. Ognjanov, *C. R. Acad. Bulgae Sci.* **13**, 51 (1960).

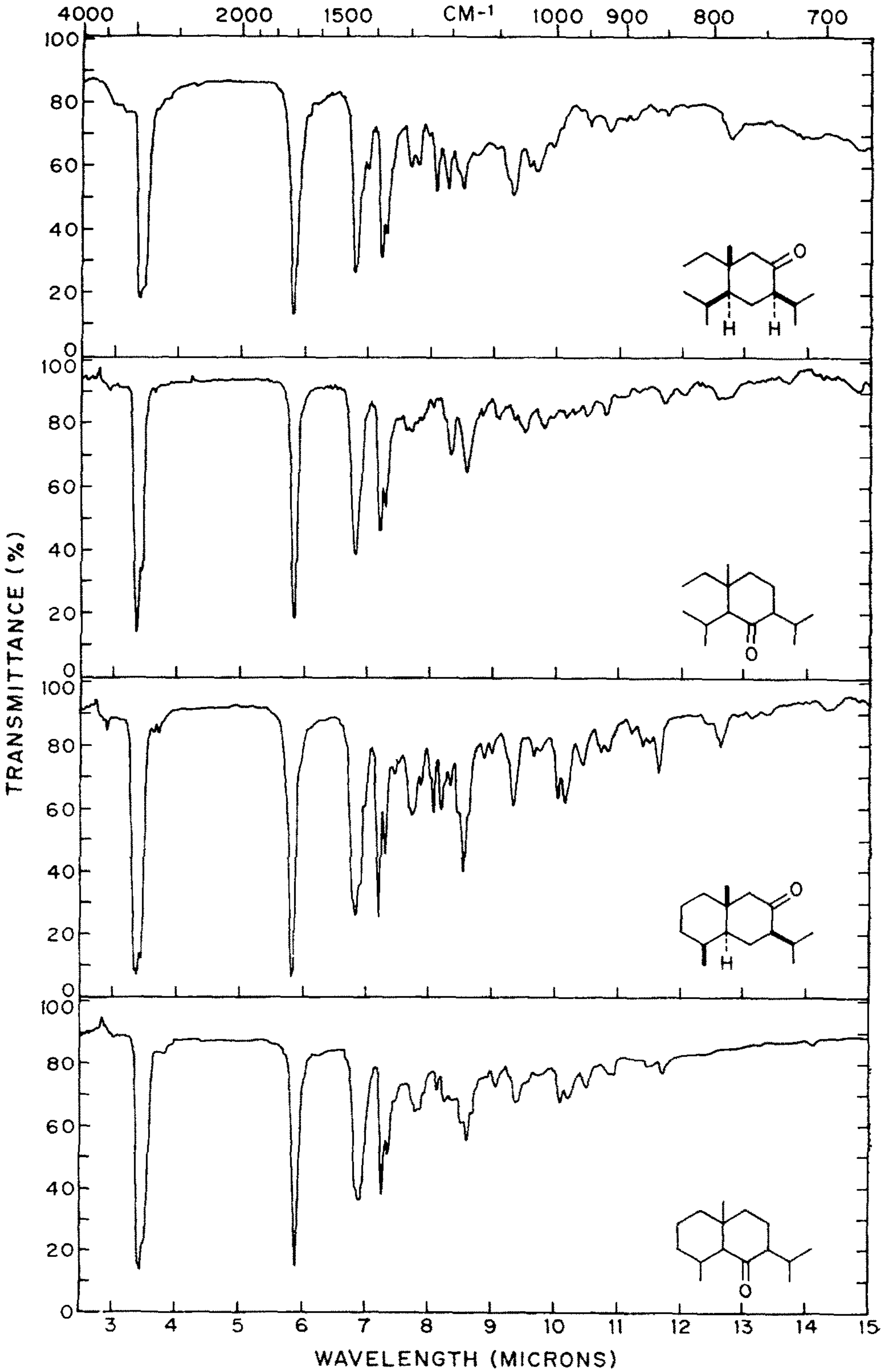
4000
2000
1500
CM-1
1000
900
800
700
100
80
60
40
20
0
TRANSMITTANCE (%)
O
H
H
O
O
H
O
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)

Fig. 1.

contained the alcohol XXVIII which was found to be pure. It had m.p. 106–107°, $(\alpha)_D^{27\cdot5}$ $+52\cdot3°$. This alcohol on oxidation gave selinane-8-one (XXIII) identical in all respects with that obtained previously by BF_3-treatment on the epoxides.

EXPERIMENTAL

M.ps are uncorrected. Rotations were determined in $CHCl_3$ solution. Light petroleum refers to fraction, b.p. 60–80°. IR spectra were measured with Perkin-Elmer (model 137-b) Infracord spectrophotometer. GLC was done on polyester column. TLC on $AgNO_3$–silica gel was done according to the method of Sukh Dev and Gupta.[7]

Isolation of elemol[1] (I). The higher boiling fraction of *Java citronella* oil was used for the isolation of elemol, m.p. 51–52°, $(\alpha)_D^{24}$ $-4\cdot73°$ (*c*, 2·3).

Hydrogenation of elemol to tetrahydroelemol[8] (II). A solution of elemol (11·8 g) in AcOH (180 ml) was hydrogenated over Adams catalyst (0·3 g) until 1 equiv. of 2·07 mole (1750 ml) H_2 was absorbed. After removal of the catalyst, the filtrate afforded tetrahydroelemol (10 g) which was purified by chromatography on grade II alumina (300 g) followed by sublimation *in vacuo*. TLC on silica gel (5% AcOEt in benzene) showed a single spot and GLC indicated a single peak, m.p. 56°, $(\alpha)_D$ $-2\cdot61°$ (*c*, 5·5). (Found: C, 78·9; H, 13·0. Calc. for $C_{15}H_{30}O$: C, 79·5; H, 10·36%.)

Dehydration of tetrahydroelemol to hydrocarbons (III and IV). To a solution of tetrahydroelemol (6·6 g) in glacial AcOH (60 ml), perchloric acid (3·3 ml; 60%) was slowly added with stirring for 72 hr at room temp. After dilution with a large excess of water and extraction with ether, extract was washed free of acid with $NaHCO_3$aq, then with water and dried over Na_2SO_4. Evaporation of the solvent gave the crude product (6·39 g) which was passed through a column of grade I alumina (180 g) and eluted with light petroleum to give a mixture of III and IV (4·65 g). It was purified by distillation over Na: b.p. 130°/8 mm, $n_D^{22\cdot5}$ 1·4715; (α_D^{23}) $-71\cdot2°$ (*c*, 8·16), $d_4^{22\cdot5}$ 0·8585; $(M)_R$ 53·80. (Found: C, 86·7; H, 13·4. $C_{15}H_{28}$ requires: C, 86·46; H, 13·54%). GLC indicated a mixture of two hydrocarbons in the ratio 80:20. TLC on $AgNO_3$–silica gel in light petroleum showed two spots of unequal intensity. NMR spectrum showed multiplet (1H) at 4·75 ($>C{=}CH$—); absence of methyl group on a double bond.

Epoxidation of the hydrocarbons III *and* IV *to the oxides* V and VI. The above mixture of hydrocarbons (1 g) was epoxidized at 0° with chloroform–benzene solution of perbenzoic acid (0·7N; 15 ml) and left overnight. The reaction mixture was extracted with ether, washed thoroughly with bicarbonate solution, water and dried. Evaporation of solvent gave the crude epoxide mixture (0·97 g) which was purified by passing through grade III alumina. The IR band at 852 cm^{-1} indicated the formation of epoxide, along with a little ketone as indicated by a band at 1724 cm^{-1}.

Treatment of epoxide mixture with BF_3–etherate

Isolation of ketones VII and VIII. BF_3–etherate (4 ml) was added dropwise to a solution of epoxides (0·97 g) in dry benzene (50 ml) at 0° and the mixture kept overnight at 5°. The product was washed with water till free from acid, dried and solvent removed. The crude ketones were passed through grade III alumina (30 g) and eluted with light petroleum to yield VII and VIII (0·75 g). GLC and TLC indicated the presence of two compounds.

The alcoholic solution of the ketones was subjected to semicarbazone formation (48 hr, room temp) and the product was chromatographed over grade II alumina (20 g). Elution with light petroleum gave VII and elution with alcohol gave the semicarbazone of VIII which was crystallized from alcohol, m.p. 174°.[3,4] (Found: N, 15·49; $C_{16}H_{31}ON_3$ requires: N, 14·9%.)

Purification of ketone (VII). This was further purified by treatment with Girard's reagent T and distillation under vacuum, b.p. 125–127° (bath)/0·5 mm, $n_D^{28\cdot5}$ 1·4695, $(\alpha)_D^{22\cdot5}$ $+36\cdot34°$ (*c*, 2·74); GLC and TLC showed a single component. IR spectrum (Fig. 1) indicated the absence of 1420 cm^{-1} band for CO—CH_2 grouping. (Found: C, 80·52; H, 12·8. $C_{15}H_{28}O$ requires: C, 80·29; H, 12·58%.)

Regeneration of the ketone (VIII). The semicarbazone (0·2 g) was mixed with oxalic acid (0·35 g) in a minimum amount of water, light petroleum (30 ml) and heated under reflux for 4 hr. The organic layer was washed with water till free from acid, dried and the solvent removed. The crude ketone was passed through grade III alumina and the light petroleum eluate was concentrated to obtain the

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[7] Sukh Dev and A. S. Gupta, *J. Chromatog.* **12,** 189 (1963).

[8] V. Sykora, V. Herout, J. Pliva and F. Sorm, *Coll. Czech. Chem. Comm.* **19,** 131 (1954).

ketone (0·152 g). It was purified by distillation *in vacuo*, b.p. 135° (bath)/1·2 mm, n_D^{28} 1·4667; $(\alpha)_D^{28}$ −5·2° (*c*, 3·2). GLC and TLC showed it to be a single component. The IR spectrum (Fig. 1) showed a band at 1420 cm^{-1} due to CO—CH$_2$ grouping and at 1712 cm^{-1} for the keto group. (Found: C, 79·62; H, 12·89. $C_{15}H_{28}O$ requires: C, 80·29; H, 12·58%.)

Semicarbazone prepared from the regenerated ketone as before had a m.p. 174°. This showed no depression with an authentic sample of the semicarbazone of hexahydropyrogermacrone prepared according to Sorm.[4]

Hydroboration of the hydrocarbons III and IV. Diborane gas was prepared by adding slowly NaBH$_4$ (4 g) in pure diglyme (40 ml) to freshly distilled BF$_3$-etherate (25 ml) in diglyme (25 ml). N$_2$ was used as the carrier gas. The diborane gas was bubbled through a solution of hydrocarbon (4·6 g) dissolved in dry tetrahydrofuran (50 ml) at 0° for 1 hr and then 1 hr at room temp. The excess diborane was decomposed by adding small pieces of ice. To this mixture was added 3N KOH (25 ml) followed by a slow addition of H_2O_2 (25 ml; 30%) and the mixture kept at room temp for 1 hr. The upper layer was separated and the aqueous layer extracted with ether. The combined ethereal extract was washed thoroughly with water, dried and solvent removed. The residue was chromatographed over grade III alumina and the light petroleum–benzene (1:2) eluate (3·41 g) showed the presence of two components on TLC. IR spectra indicated the presence of —OH grouping.

Acetylation of the above material. The light petroleum–benzene fraction (3·41 g) was acetylated with acetic anhydride (1 ml) in pyridine (10 ml) at room temp (24 hr). The acetyl derivative (3·38 g) was passed through grade III alumina and eluted with light petroleum and ether. The light petroleum eluate (1·63 g) indicated it to be entirely the acetyl derivative, while the ether fraction (1·74 g) showed in addition the presence of —OH grouping. The acetyl compound (1·63 g) was passed through silica gel (48 g) column and eluted with light petroleum–benzene (75:25) and collected in 30 fractions of 5 ml each followed by ether.

Light petroleum–benzene fraction

Preparation of VIII. TLC analysis of the first fifteen fractions showed essentially a single component. These were mixed (0·5 g), hydrolysed by alkali and the alcohol purified by distillation, b.p. 130° (bath)/0·9 mm, $(\alpha)_D^{28}$ +14·74° (*c*, 1·69). (Found: C, 79·68; H, 13·3. $C_{15}H_{30}O$ requires: C, 79·57; H, 13·36%.)

The hydroxy compound (0·49 g) was oxidized to VIII by Jones reagent. The crude ketone (0·3 g) was passed through grade III alumina and the light petroleum eluate gave the pure ketone (0·25 g). IR spectrum showed a band at 1420 cm^{-1}. The pure semicarbazone had m.p. 174°, undepressed when mixed with semicarbazone obtained previously. The regenerated ketone was purified by distillation (0·2 g), b.p. 130° (bath)/1·1 mm, n_D^{25} 1·4662; $(\alpha)_D^{25}$ −4·2° (*c*, 2·6); GLC and TLC showed it to be only one compound. (Found: C, 80·8; H, 12·75. $C_{15}H_{28}O$ requires: C, 80·29; and H, 12·58%.)

Ether fraction

Isolation of VIII. The ether fraction (0·45 g) was rechromatographed on grade II alumina (13·5 g) and eluted with light petroleum–benzene (1:1) in 5 fractions of 10 ml each. Fractions 1 and 2 (0·24 g) which showed a single component on TLC were combined, hydrolysed and the alcohol obtained (b.p. 130° (bath)/0·9 mm) oxidized by Jones reagent to VIII. This was purified by the preparation of semicarbazone m.p. 174°. Regenerated ketone, b.p. 135° (bath)/1·2 mm, n_D^{28} 1·4667; IR band at: 1710 cm^{-1} for carbonyl, and 1420 cm^{-1} (—CO—CH$_2$).

Hydrogenation of eudesmol to dihydroeudesmol (XVII). A solution of eudesmol (13·5 g) in glacial AcOH (100 ml) was hydrogenated over PtO$_2$ (0·3 g). The product was passed through grade II alumina (400 g) and eluted with light petroleum–beznene (1:1) to yield the dihydroproduct (12·2 g) which was further purified by sublimation, m.p. 81° (GLC single peak).

Dehydration of dihydroeudesmol to hydrocarbons (XVIII and XIX). Dihydroeudesmol (10 g) in glacial AcOH (80 ml) was dehydrated with perchloric acid (4·5 ml; 60%). The crude material (9·7 g) was passed through grade I alumina (300 g) and eluted with light petroleum. The eluate (7·53 g) was distilled over Na, b.p. 125–128°/3 mm, $(\alpha)_D^{28\cdot5}$ −20·04° (*c*, 13·7); GLC and TLC indicated the presence of two compounds.

Epoxidation of hydrocarbons XVIII and XIX. The above mixture of hydrocarbons (1 g) was epoxidized. The oxide (0·89 g) was purified by passing through grade III alumina. The IR spectrum showed a band at 852 cm^{-1} for an epoxide.

Treatment of the epoxide mixture XX and XXI *with BF_3–etherate.* BF_3–etherate (4 ml) was added dropwise to a solution of epoxides (0·89 g) in dry benzene (50 ml) at 0° and the mixture kept overnight at 5°. The crude mixture of ketones XXII and XXIII were separated via their semicarbazones.

Ketone XXII had b.p. 105–110° (bath)/0·5 mm, n_D^{20} 1·4882; GLC analysis showed that about 40% of the product corresponded to dihydrojunenone. The IR spectrum indicated the absence of the band at 1420 cm^{-1} for the CO—CH_2 grouping and was almost similar to dihydrojunenone. (Found: C, 81·8; H, 12·1. $C_{15}H_{26}O$ requires: C, 81·02; H, 11·79%.)

The ketone XXIII had b.p. 138–140° (bath)/0·2 mm, n_D^{20} 1·4840; $(\alpha)_D^{29}$ −21·1° (*c*, 2·13); GLC and TLC indicated a single peak and spot respectively. The IR spectrum (Fig. 1) indicated the presence of the band at 1420 cm^{-1} for —CO—CH_2 grouping and a carbonyl band at 1712 cm^{-1}. (Found: C, 80·48; H, 11·76. $C_{15}H_{26}O$ requires: C, 81·02; H, 11·79%); semicarbazone, m.p. 197–198°. (Found: N, 14·73. $C_{16}H_{29}ON_3$ requires: N, 15·04%.)

Hydroboration of the hydrocarbons XVIII *and* XIX. The hydrocarbons (4 g) gave the reaction product (3·7 g) which was passed through grade III alumina (120 g) and eluted with light petroleum–benzene (1:2). The eluate on concentration left a residue (3·52 g) which was passed through silicic acid column (30 g) and eluted with benzene in 25 fractions of 10 ml each. The first 5 fractions showed on GLC and TLC 4 compounds, one of which corresponded to dihydrojunenol. Attempts to separate in a pure state either by column chromatography or preparative TLC did not give pure dihydrojunenol.

Isolation of the alcohol XXVIII. Fractions 10 to 25 were essentially one compound as indicated by GLC and TLC analysis. Fractions 10 to 15 were mixed and crystallized from light petroleum to a constant m.p. 106–107°, $(\alpha)_D^{27\cdot5}$ +52·3° (*c*, 1·11%). (Found: C, 80·26; H, 12·89. $C_{15}H_{28}O$ requires: C, 80·29; H, 12·58%.)

Conversion of XXVIII *to the ketone* XXIII. The alcohol (XXVIII) was oxidized with Jones reagent to yield XXIII. The IR spectrum indicates the presence of 1420 cm^{-1} for CO—CH_2 and 1712 cm^{-1} for the keto group. The ketone had b.p. 142° (bath)/0·5 mm, n_D^{20} 1·4840; $(\alpha)_D^{29\cdot5}$ −21·18° (*c*, 3·2). (Found: C, 80·48; H, 11·76. $C_{15}H_{26}O$ requires: C, 81·02; H, 11·79%.) Semicarbazone, m.p. 197–198°, which showed no depression with that obtained by BF_3–etherate treatment on the epoxide.