Tetrahedron, 1964, Vol. 20, pp. 1289 to 1300. Pergamon Press Ltd. Printed in Northern Ireland

TERPENOIDS—XLVIII

STRUCTURE AND STEREOCHEMISTRY OF HYDROXYVALERANONE AND ACETYLHYDROXYVALERANONE*

K. S. KULKARNI, S. K. PAKNIKAR and S. C. BHATTACHARYYA
National Chemical Laboratory, Poona, India

(*Received* 23 *December* 1963)

Abstract—Two new sesquiterpenes, hydroxyvaleranone and its acetyl derivative, have been isolated from Indian valerian root oil (*Valeriana wallichi*). On the basis of NMR spectral results along with other spectroscopic, analytical and chemical data, structure I has been assigned to hydroxyvaleranone. ORD data and chemical evidences also indicate that it is represented by the stereoformula XXIII.

IN continuation of our work[1] on the isolation and characterization of the constituents of Indian valerian oil (*Valeriana wallichi*), we have isolated a crystalline keto-alcohol, the structure (I) and stereochemistry (XXIII) of which are described in the present communication. It belongs to the rather uncommon valerane group of which valeranone[2] is the only known member. It is proposed to name this keto-alcohol hydroxyvaleranone† because of its close structural relationship with valeranone.

The alcohol was isolated from the fraction N_3[1] in which it occurs in the free state as well as in the form of its acetate. It is represented by the molecular formula, $C_{15}H_{26}O_2$ and is saturated towards tetranitromethane and catalytic hydrogenation.

The IR spectrum of hydroxyvaleranone (Fig. 1) showed bands at 3472 and 1692 cm^{-1} attributed to a hydroxy function and a carbonyl group respectively on a 2,2-alkyl substituted[3] cyclohexanone. A weak band at 1412 cm^{-1} suggests the presence of a $-\overset{\overset{O}{\|}}{C}-CH_2-$ grouping which is further supported by its NMR spectrum. The IR and NMR spectra of this keto-alcohol show a striking similarity to those of valeranone (IV) and suggest that the newly isolated keto-alcohol may be a hydroxy derivative of valeranone.

* Communication No. 651 from the National Chemical Laboratory, Poona-8, India.

† In a recent issue of the Japanese journal *Chem. Pharm. Bull.* **11** (9), 1210–12 (1963) just received in our laboratory, it is found that the same alcohol in the form of its acetate has been isolated from Japanese valerian root oil. The Japanese authors also arrived at the same conclusions regarding its structure and stereochemistry by adopting an almost identical procedure. Our results were essentially concluded several months ago and discussed in our communications with Prof. W. Klyne, Westfield College, London, regarding stereochemistry since July 1963. These results have also been presented at the Symposium on *Physical Methods in Organic Structure Determination* held in the National Chemical Laboratory, Poona, India, on 5th, 6th and 7th Dec. 1963.

[1] Terpenoids XLVI: *Tetrahedron* **20**, 963 (1964).

[2] J. Krepinsky, M. Romanuk, V. Herout and F. Sorm, *Coll. Czech. Chem. Comm.* **27**, 2638 (1962) and references cited therein.

[3] E. J. Corey, T. H. Topie and W. A. Woznaik, *J. Amer. Chem. Soc.* **77**, 5415 (1955).

In order to test this assumption, it was hoped that hydrogenolysis of the keto-tosylate (II) with lithium aluminium hydride followed by oxidation with Jones reagent[4] would produce valeranone. Although, the tosyl derivative formed according to expectation, its reduction with lithium aluminium hydride results in a diol (IIIa) as the reaction with lithium aluminium hydride proceeds exclusively at the sulphur atom.[5]

Since dehydrogenation of valeranone, valeranol and valerene,[2,6] is known not to yield any useful information about the basic skeleton, the dehydrogenation experiments were not, at first, attempted but proof of the valerane skeleton (VI) was established as follows. Hydroxyvaleranone (I) was oxidized with CrO_3–pyridine complex

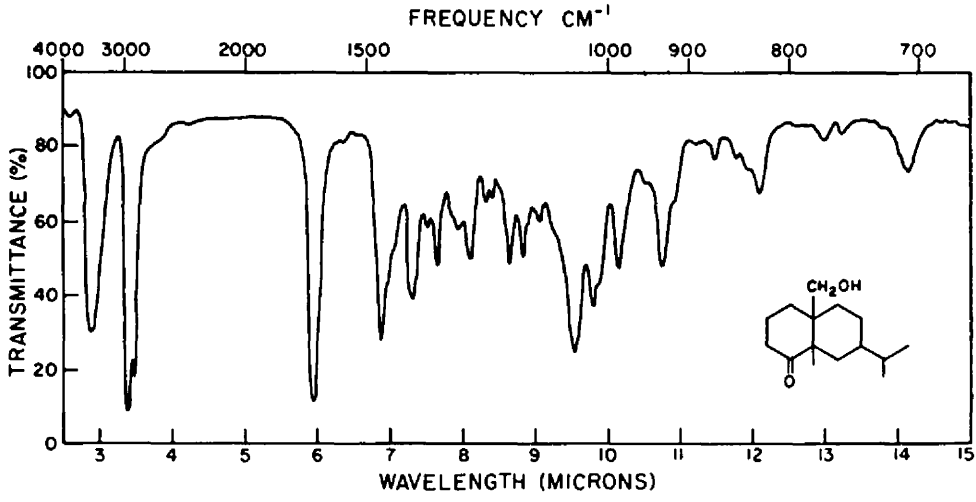


FIG. 1. IR Spectrum (nujol) of hydroxyvaleranone

to the keto-aldehyde (V, IR bands 2703, 1709 and 1692 cm^{-1}) which without isolation was subjected to Wolff–Kishner reduction to give valerane (VI), identical in all respects (IR, optical rotation, mixed VPC) with the authentic sample prepared from valeranone. The formation of the keto-aldehyde (V) indicates that the hydroxy group present in hydroxyvaleranone is primary in nature.

In order to establish the position of the carbonyl group, hydroxyvaleranone (I) was converted to valeranone (IV) in accordance with the reactions given in Chart I.

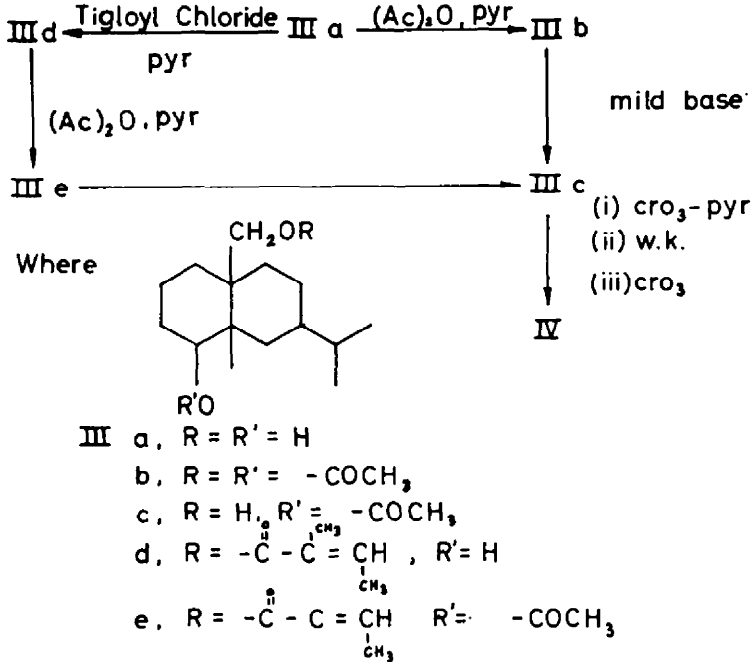
All attempts to obtain the diol monoacetate (IIIc) by partial hydrolysis were unsuccessful but IIIc was obtained by the application of a slight modification. The diol (IIIa) on reaction with tigloyl chloride affords the monotiglate (IIId) which on mild acetylation gives the diester (IIIe). Osmium tetroxide-periodic acid treatment of IIIe removes the tiglate group yielding the desired diol monoacetate (IIIc). But as the yields were so poor, conversion of the diol-monoacetate to valeranone was not attempted.

[4] K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.* 39 (1946); C. Djerassi, R. R. Ingle and A. Bowers, *J. Org. Chem.* **21**, 1547 (1956).

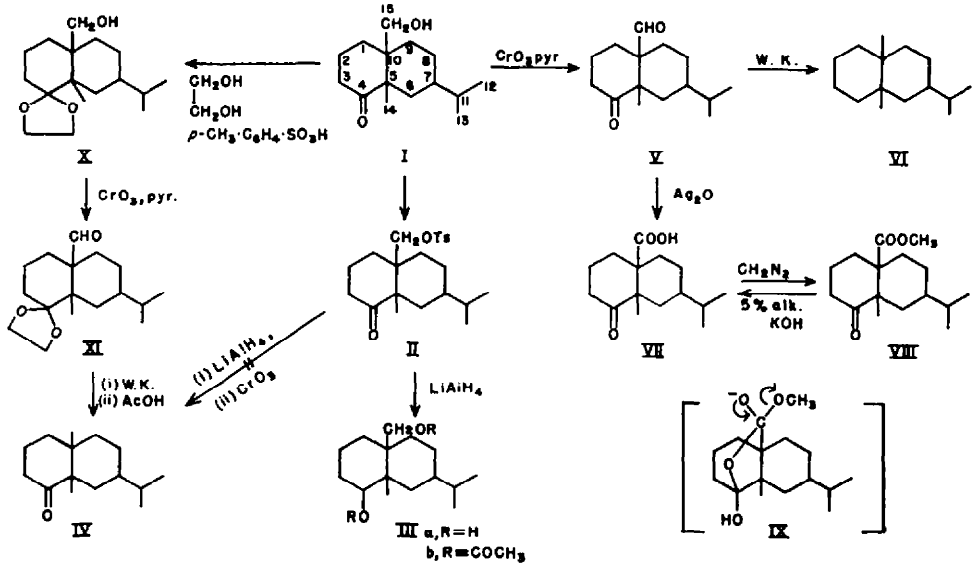
[5] H. Schmid and P. Karrer, *Helv. Chim. Acta* **32**, 1371 (1949); D. H. R. Barton and C. J. W. Brooks, *J. Chem. Soc.* 257 (1951).

[6] T. R. Govindachari, B. R. Pai, K. K. Purushothaman and S. Rajadurai, *Tetrahedron* **12**, 105 (1961).

CHART I



Hydroxyvaleranone (I) was finally converted to valeranone (IV) in the following way. Treatment with ethylene glycol and *p*-toluenesulphonic acid in refluxing benzene, yields the ethylene ketal (X) oxidation of which with chromium trioxide–pyridine complex[7] gives the ketal-aldehyde (XI), which without further purification was reduced by Wolff–Kishner method and the resulting ketal hydrolysed to yield



[7] G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *J. Amer. Chem. Soc.* 75, 422 (1953).

valeranone (IV), identified by mixed m.p. of the semicarbazone and superimposable IR spectra (Fig. 2).

In order to determine the relative positions of the carbonyl and hydroxyl groups in hydroxyvaleranone, the keto-aldehyde (V) was oxidized with silver oxide to the keto-carboxylic acid (VII), characterized as its methyl ester (VIII). Generally, sterically hindered carbomethoxy groups are difficult to hydrolyse. In contrast, the ketoester (VIII) can be saponified easily, by refluxing with 5% methanolic potassium

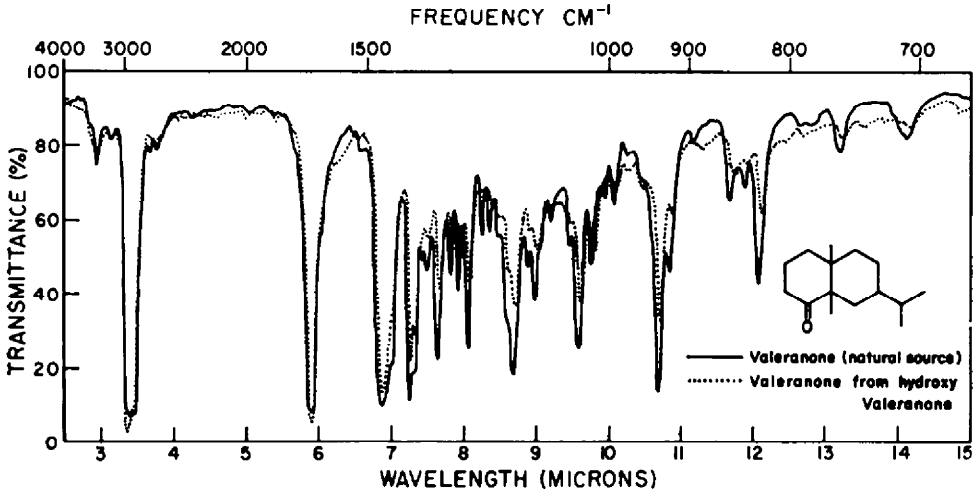
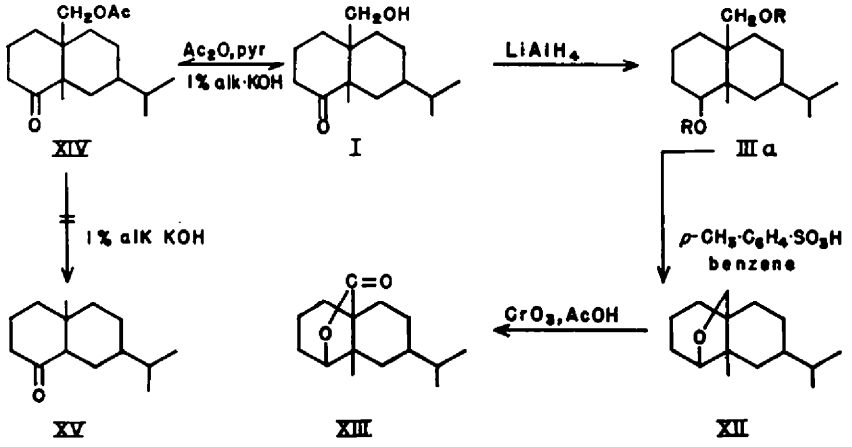


FIG. 2

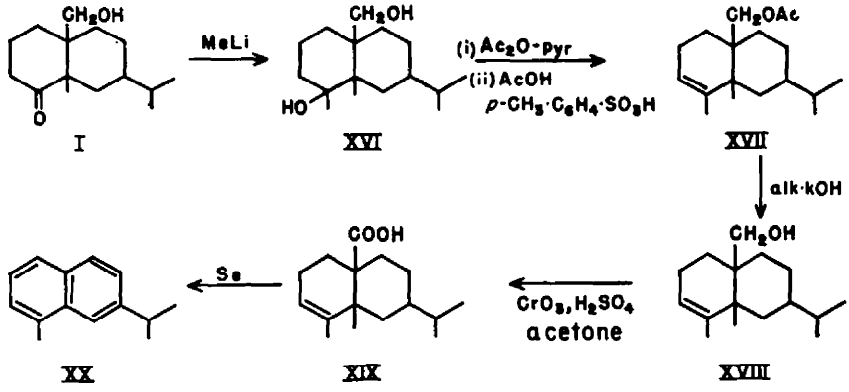
hydroxide, to a crystalline keto-carboxylic acid (VII). The easy hydrolysis of the carbomethoxy group in VIII is analogous to the hydrolysis of methyl machaerate,[8] and is due to the activating influence of a carbonyl group in γ-position (intermediate IX). The keto-ester (VIII) cannot be a β-keto-ester as alkaline hydrolysis would cause decarboxylation to a nor-ketone (XV). The possibility of a 1,3-relationship of the carbonyl group to the primary hydroxyl function was further eliminated in the



[8] C. Djerassi and A. E. Lippman, *J. Amer. Chem. Soc.* 77, 1825 (1955).

following way. Mild alkaline hydrolysis of the acetyl derivative yields the keto-alcohol (I) and not the nor-ketone (XV) formed by the elimination of formaldehyde by a retro-aldol reaction.[9]

Reduction of hydroxyvaleranone with lithium aluminium hydride, gives the crystalline diol (IIIa), which forms the diacetate (IIIb) upon mild acetylation. The diol (IIIa) in benzene containing catalytic amount of *p*-toluenesulphonic acid is easily converted to the oxide (XII), the IR spectrum of which shows a band at 1488 cm^{-1}, typical of a —CH_2—O—C— grouping present in many 6β-19-oxido-steroids.[10] On chromic acid oxidation at 80°, the lactone (XIII) is produced, which from its IR absorption at 1770 cm^{-1} was proved to be a γ-lactone. The oxide ring in (XII) should therefore be five membered.



Treatment of hydroxyvaleranone (I) with methyl-lithium, affords the crystalline diol (XVI), which after protection of the primary hydroxyl group by acetylation may be dehydrated to the unsaturated acetate (XVII). The alcohol (XVIII) obtained by alkaline hydrolysis of this acetate on oxidation with Jones reagent yields the unsaturated acid (XIX). Dehydrogenation of this acid with selenium gave an aromatic product in poor yield but was identified as eudalene (XX) by spectral data and VPC analysis. The carbonyl group in hydroxyvaleranone and hence in valeranone is, therefore, located at C_4.

Based on these experiments, hydroxyvaleranone should be represented by the structure (I), which is fully supported by the NMR data.

The NMR spectra[11] (Fig. 3) of hydroxyvaleranone (I) and valeranone (IV) are strikingly similar except that the former shows the presence of only one quartenary methyl group[12] and two hydrogens attached to a carbon bearing the hydroxy group.

[9] D.H. R. Barton and P. de Mayo, *J. Chem. Soc.* 887 (1954); C. Djerassi and W. Rittel, *J. Amer. Chem. Soc.* **79**, 3528 (1957).

[10] J. F. Bagli, P. F. Morand and R. Gaudry, *J. Org. Chem.* **28**, 1207 (1963).

[11] NMR spectra were measured in CCl_4 using TMS as internal standard on a Varian Model Spectrometer at 60 mc/s. The chemical shifts are expressed in 'δ' units. We wish to thank Dr. P. M. Nair and his colleagues of this laboratory for the NMR measurements.

[12] Comparison of the c-methyl values of hydroxyvaleranone and valeranone further supports this assignment.

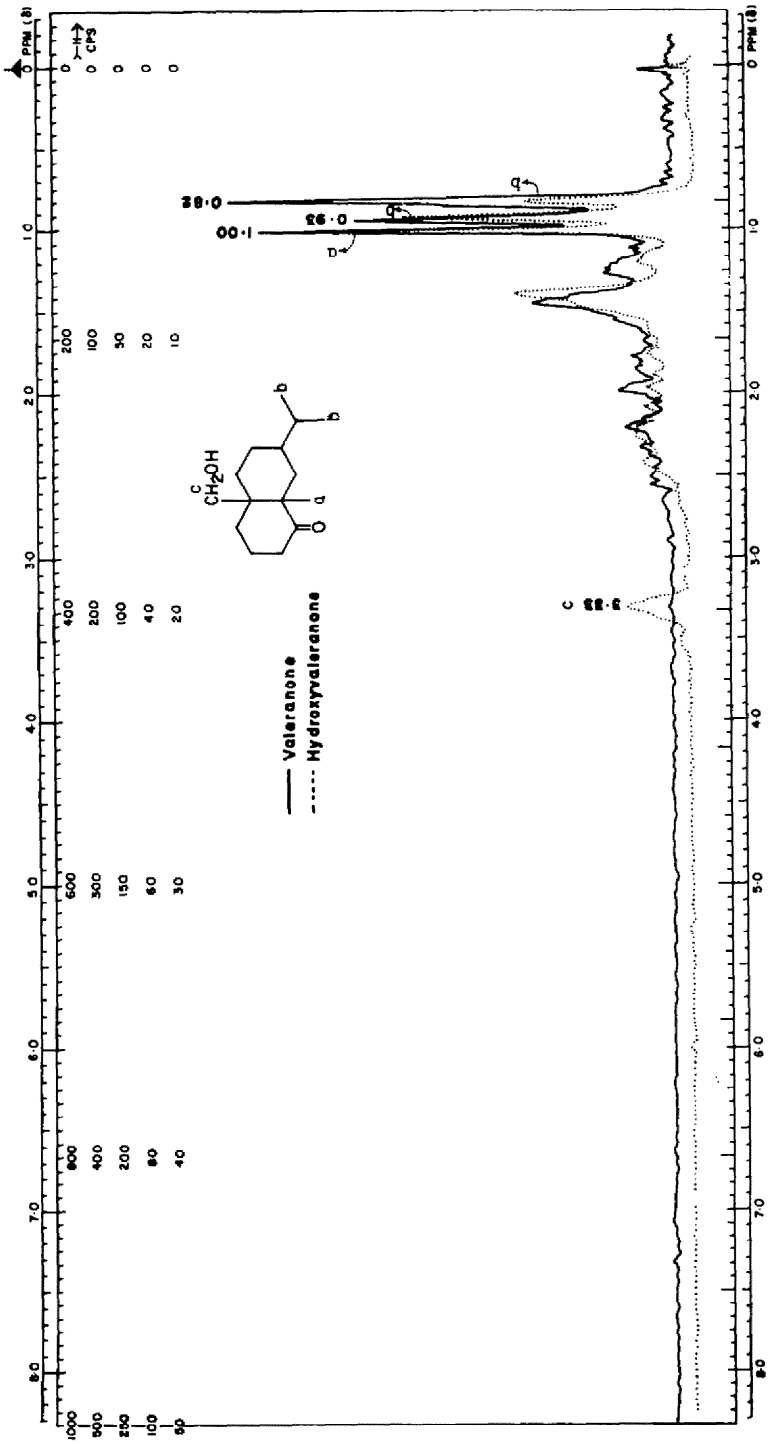


FIG. 3. NMR spectra of hydroxyvaleranone and valeranone.

The unresolved peak centered at δ 3·33 is due to the methylene hydrogens of the —CH_2OH group, further confirmed by a downfield shift of 0·47 ppm upon acetylation.[13] The NMR spectrum of the acetyl derivative (Fig. 4) shows a typical non-equivalence quartet (δ 3·8, J, 11 c/s) characteristic of a quaternary acetoxy methyl group. The NMR spectrum of the oxide (XII) shows a doublet (6H) centered at δ 0·9 (J, 5·5 c/s, $(CH_3)_2CH$—), singlet (3H) at δ 1·03 (CH_3—C<) and a multiplet (3H) in the 3·25 to 3·8 δ region (—CH_2—O—CH—).

Based on the experiments together with the data available in the literature, some conclusions can be drawn concerning the stereochemistry of hydroxyvaleranone.

The ring fusion in hydroxyvaleranone may be regarded as '*cis*' for the following reasons.

According to Kripinsky *et al.*,[2] valeranone (IV) on Bayer–Villiger oxidation affords a lactone which on basic hydrolysis and esterification yields the hydroxy-ester (XXI). The latter on dehydration with thionyl chloride in pyridine gives the corresponding unsaturated methyl ester which contains at least 50% XXII. Since Bayer–Villiger oxidation proceeds with the retention of the configuration[14] and the mode of dehydration[15] shows that the tertiary hydroxyl group in XXI must be equatorial and hence the C_5 methyl must be axial with respect to the ring containing the isopropyl side chain.

In compounds with A/B *trans* junction, the aldehyde group at C_{10} (comparable to C_{19} substituent in steroids) is highly hindered and very difficult to reduce even under modified Wolff–Kishner conditions.[16] As no difficulty was observed in the reduction of the keto-aldehyde (V) or the ketal aldehyde (XI) by the Wolff–Kishner method, the aldehyde group in V and hence the hydroxymethyl group in I may be regarded as equatorial.

The ORD curve* of hydroxyvaleranone (I) shows a strong negative cotton effect and is practically superimposable (Fig. 5) upon that of valeranone (IV). As hydroxyvaleranone (I) may be converted to valeranone (IV), it is clear that both the compounds possess the same stereochemistry at all the centres of asymmetry.

Assuming the two all-chair conformations with the isopropyl substituent equatorial, hydroxyvaleranone should be represented by one of the following stereochemical structures (XXIII to XXVI).

Structures XXV and XXVI are eliminated, because the C_5 methyl substituent becomes equatorial with respect to the ring having the isopropyl substituent. Finally structure XXIII has been preferred over XXIV because of the observed strong –ve cotton effect.

The stereochemical features were further clarified by converting valeranone by a

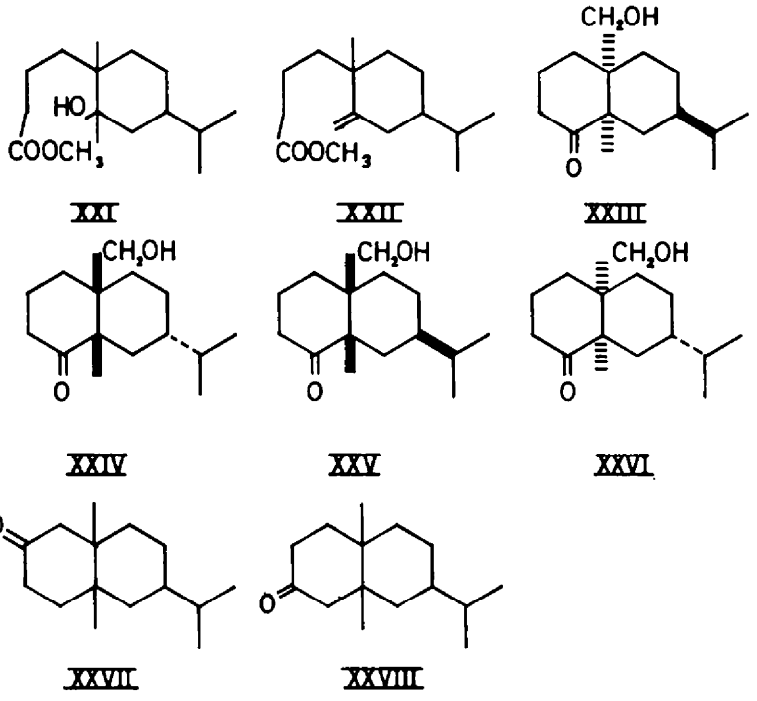
* We are grateful to Prof. W. Klyne, Westfield College, University of London, for the ORD measurements and valuable discussion.

[13] L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* p. 55, Pergamon Press, London (1959).

[14] R. B. Turner, *J. Amer. Chem. Soc.* **72**, 878 (1950); T. F. Gallagher and T. H. Kritchevsky, *J. Amer. Chem. Soc.* **72**, 882 (1950).

[15] D. H. R. Barton, A. Da S. Campos-Neves and R. C. Cookson, *J. Chem. Soc.* 3500 (1956) and references cited therein.

[16] H. Vorbruggen and C. Djerassi, *Tetrahedron Letters* **3**, 119 (1961).



series of reactions to the ketones XXVII and XXVIII, the ORD studies* of which throw light on the stereochemistry of valeranone and consequently that of hydroxyvaleranone.

The chromatographic fractions eluted earlier than hydroxyvaleranone afforded another substance having the molecular formula $C_{17}H_{28}O_3$. The IR spectrum of a purified sample exhibits bands at 1733 and 1244 cm^{-1} due to an acetoxy group and at 1699 cm^{-1} due to a ketone on a six-membered ring, and is identical with the IR spectrum of the acetyl derivative of hydroxyvaleranone. This was further confirmed by the NMR spectra and its alkaline hydrolysis to hydroxyvaleranone.

EXPERIMENTAL†

M.ps are uncorrected. Specific rotations were determined in chloroform solution unless otherwise stated. UV absorption spectra were measured in ethanol with a Beckman Model DK-2 spectrophotometer. IR spectra were taken with the Perkin-Elmer (Model 137b) Infracord Spectrophotometer. VPC analyses were carried out using at least two stationary phases employing a Griffin MK-II model and Perkin–Elmer analyser.

Isolation of hydroxyvaleranone (I). Hydroxyvaleranone was obtained by careful chromatography of the neutral fraction N_3 of Indian valerian root oil.[1] The IR spectrum of the tail chromatographic fractions showed the presence of hydroxyl and carbonyl functions. The above crude fraction (10 g) was treated in alcoholic solution in the usual way with semicarbazide hydrochloride and sodium acetate and the solution allowed to stand overnight. The semicarbazone (1·5 g from 1·5 kg of the oil) was recrystallized from ethanol m.p. 192–93° (Found: N, 14·2. $C_{16}H_{29}O_3N_3$ requires: N, 14·23%). Hydroxyvaleranone was obtained as a colourless oil when regenerated from the semicarbazone by

* By a series of reactions, similar to those adopted by Japanese workers, we have also arrived at the same conclusions by submitting Maaliol and β-eudesmol to degradative reactions.

† The authors wish to thank Mr. V. S. Pansare and colleagues Mr. H. Gopinath and Mr. K. G. Deshpande for microanalyses and spectroscopic measurements and Mr. B. V. Bapat and Dr. V. G. Naik for VPC analyses.

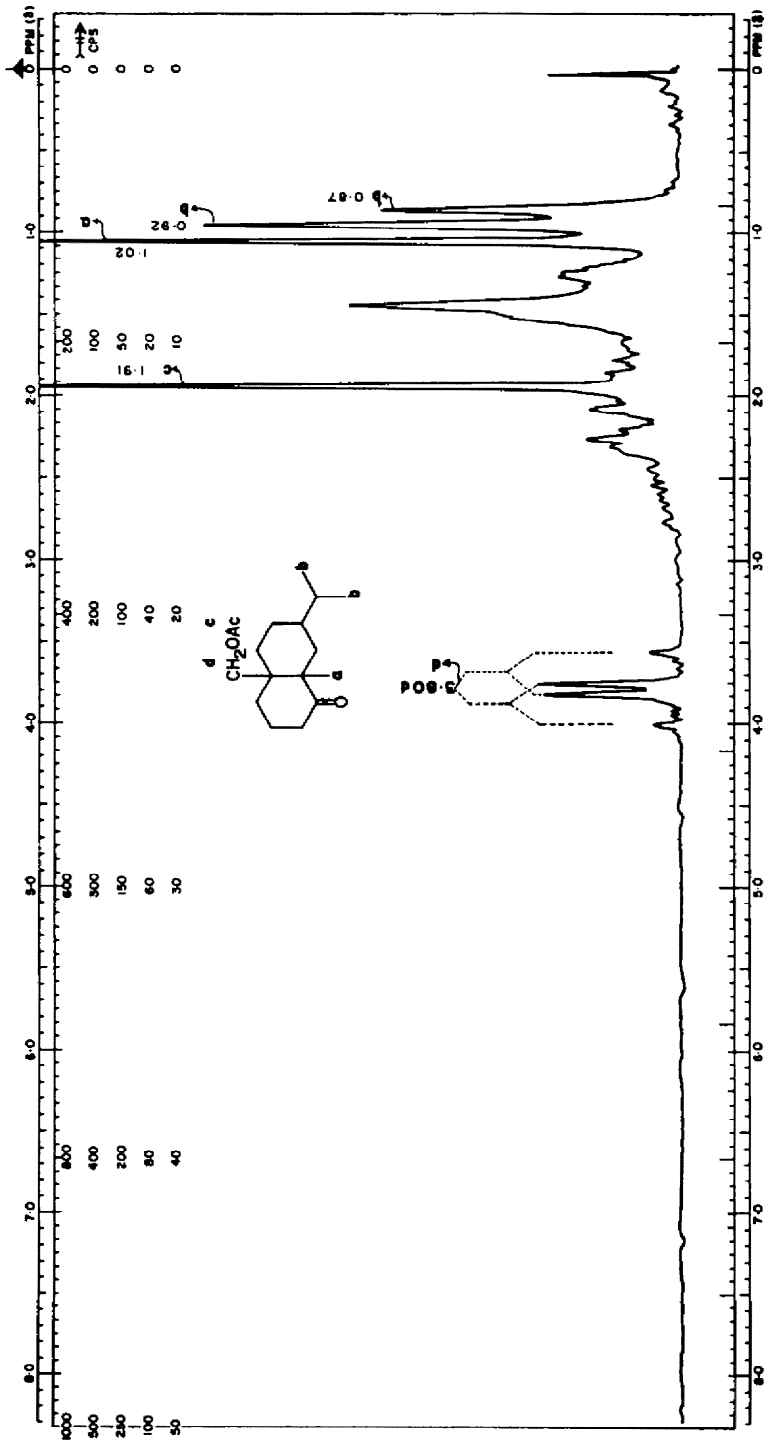


FIG. 4. NMR spectrum of acetylhydroxyvaleranone.

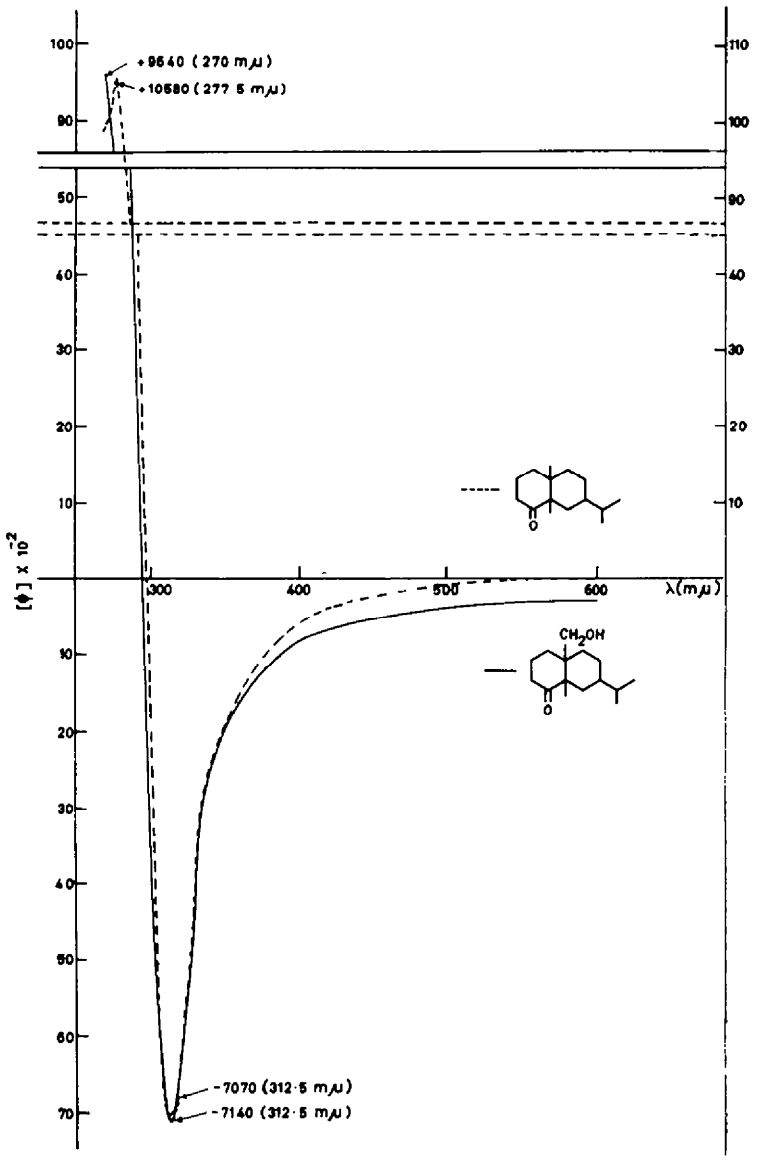


FIG. 5. ORD curves of valeranone and hydroxyvaleranone.

oxalic acid–light petroleum procedure. The product solidified on standing and was further purified by sublimation *in vacuo*. VPC analysis showed it to be composed of one component only, m.p. 52–53°, $(\alpha)_D$ −72° (*c*, 5·8), λ_{max} 290 mμ (ε 50) (Found: C, 75·6; H, 11·09. $C_{15}H_{26}O_2$ requires: C, 75·58; H, 11·0%; C—CH_3 6·65%, the same for valeranone 7·7%). It gave a negative test with tetranitromethane and was stable towards hydrogenation in acetic acid and platinum oxide.

Acetate of hydroxyvaleranone (XIV). Acetylation of I (91 mg) with acetic anhydride (2 ml) in pyridine (5 ml) at room temp. afforded the acetate, b.p. 180–85° (bath)/0·3 mm, $(\alpha)_D$ −55·5° (*c*, 1·8) (Found: C, 73·02; H, 10·36. $C_{17}H_{28}O_3$ requires: C, 72·82; H, 10·02%). IR bands at: 1733, 1699, 1235 and 1042 cm^{-1}.

Valerane (VI) *from hydroxyvaleranone* (I). A cold solution of hydroxyvaleranone (290 mg) in pyridine (10 ml) was added slowly to a slurry of CrO_3–pyridine complex (prepared from 300 mg CrO_3 and 10 ml pyridine) at 0°, and the mixture kept overnight at room temp. The crude keto-aldehyde

(V, 250 mg) obtained showed IR absorption at 2703 and 1709 cm^{-1} due to aldehyde carbonyl and 1692 cm^{-1} due to a six-membered ring ketone. The product without further purification was subjected to Wolff–Kishner reduction.

A mixture of the above keto-aldehyde (225 mg), diethylene glycol (10 ml), KOH (0·6 g) and hydrazine hydrate (0·6 ml, 100%) was heated under reflux for 4 hr (in a N_2 atm.). Dilution with water and extraction with ether afforded an oil (134 mg) which was chromatographed on alumina (Grade I, 5 g). Elution with light petroleum furnished the saturated hydrocarbon valerane as a colourless mobile oil (70 mg), b.p. 120° (bath)/10 mm, n_D^{31} 1·4790, $(\alpha)_D$ +44·5° (*c*, 2·0) (Found: C, 86·18; H, 13·24. $C_{15}H_{28}$ requires: C, 86·46; H, 13·54%). Identity was further established by mixed VPC (single peak) and comparison of the IR spectra with an authentic sample of valerane prepared by Wolff-Kishner reduction of valeranone.

Diol (IIIa) *from hydroxyvaleranone* (I). Hydroxyvaleranone (116 mg) in dry ether (25 ml) was refluxed with $LiAlH_4$ (200 mg in 25 ml of dry ether) and the crude diol, m.p. 145–150° (109 mg) was recrystallized from benzene, m.p. 153–154°, $(\alpha)_D$ +50°(*c*, 0·5). (Found: C, 74·47; H, 11·84. $C_{15}H_{28}O_2$ requires: C, 74·95; H, 11·74%). IR bands at: 3425, 1449, 1374, 1368, 1220, 1175, 1104, 1050, 1026, 980, 961, 936, 914, 877, 847, 826 cm^{-1}.

The diacetate (IIIb) was obtained by treatment of the diol with the requisite quantity of pyridine–acetic anhydride at room temp for 24 hr. The IR spectrum showed the fully acetylated nature of the product. An attempt to partially hydrolyse it with 0·04 N alcoholic potash resulted in the regeneration of the parent diol, m.p. 153–154°.

Details regarding tigloylation[17] and other reactions described in the text are not given as these results were not useful for preparative purposes.

Oxide (XII) *from diol* (IIIa). A solution of diol (100 mg) in benzene (10 ml) and *p*-toluenesulphonic acid monohydrate (30 mg) was heated under reflux for 40 min and after cooling, the benzene solution was washed with $NaHCO_3$ aq. Removal of solvent and filtration through a short column of alumina (grade II, 5 g) and elution with light petroleum afforded the oxide as a colourless mobile oil (70 mg), n_D^{27} 1·4962 (Found: C, 81·02; H, 12·09. $C_{15}H_{26}O$ requires: C, 81·02; H, 11·79%). IR bands at: 1488, 1460, 1374, 1361, 1316, 1292, 1253, 1232, 1211, 1190, 1163, 1149, 1076, 1042, 1020, 1002, 954, 934, 903, 886, 863, 846, 837, 781 and 741 cm^{-1}. VPC analysis showed it to be composed of one component only.

Lactone (XIII) *from oxide* (XII). The oxide (20 mg) in glacial acetic acid (5 ml) was oxidized with chromic acid (20 mg) dissolved in acetic acid (2 ml). The mixture was heated on a water bath (70–80°) for 15 min and after cooling methanol was added. The product after processing in the usual manner afforded an impure lactone (15 mg). Although the lactone could not be isolated in pure form (*vide infra*) due to paucity of material, a strong band at 1770 cm^{-1} in the IR spectrum proved it to be a γ-lactone.

Keto-tosylate (II) *from hydroxyvaleranone* (I). Treatment of keto-alcohol (I, 75 mg) with *p*-toluenesulphonyl chloride in pyridine at 0° for 24 hr and working up in the usual way afforded the tosylate (II, 70 mg). IR bands at: 1701, 1592, 1460, 1362, 1242, 1212, 1189, 1176, 1099, 1047, 1020, 961 (broad), 934, 877, 800 (broad) and 724 cm^{-1}.

Reduction of the tosyl derivative with $LiAlH_4$ gave the diol, m.p. 153–154°.

Valeranone (IV) *from hydroxyvaleranone* (I). A mixture of hydroxyvaleranone (200 mg), ethylene glycol (5 ml), benzene (50 ml) and *p*-toluenesulphonic acid monohydrate (50 mg) was heated under reflux for 24 hr. The product after usual work up afforded the ketal-alcohol (190 mg), n_D^{25} 1·4975, b.p. 165–170° (bath)/1 mm. (Found: C, 73·2; H, 10·77. $C_{17}H_{30}O_3$ requires: C, 72·3; 10·71%). IR bands at: 3448, 1385, 1368, 1337, 1282, 1190, 1147, 1109, 1075, 1031, 989, 961, 912, 885, 837 and 767 cm^{-1}.

A solution of the above ketal-alcohol (160 mg) in pyridine (10 ml) was oxidized with CrO_3–pyridine complex (prepared from 200 mg of CrO_3 and 8 ml pyridine) to yield the ketal-aldehyde (XI, 150 mg), which without isolation was reduced under the Wolff–Kishner conditions using diethylene glycol (20 ml), hydrazine hydrate (1 ml, 98%) and KOH (0·5 g). The residue obtained after the usual work up, was dissolved in ether, and treated with 10 ml 70% acetic acid and the solution heated on steam bath for 20 min for deketalization and the product filtered through alumina (grade II, 10 g). Light petroleum benzene (1:1) eluted 91 mg valeranone, semicarbazone m.p. 204°, mixed m.p. with valeranone semicarbazone 203–204°. VPC of this material alone or mixed with authentic

[17] S. M. Kupchan, A. D. J. Balon and E. Fujita, *J. Org. Chem.* **27**, 3103 (1962).

sample of valeranone showed only one peak and the IR spectrum identical with that of valeranone from natural sources.

Keto-carboxylic acid (VII) *from keto-aldehyde* (V). The keto-aldehyde (200 mg) and silver nitrate (0·6 g; analytical grade) were dissolved in absolute alcohol and a solution of NaOH (0·3 g) in aqueous ethanol (1:9, 10 ml) was added dropwise with stirring and the mixture allowed to stand overnight at room temp. It was then diluted with water and acidified with dil. H_2SO_4 aq. and extracted with ether. Removal of solvent yielded a gummy product, which was directly converted to its methyl ester (VIII) by treatment with excess of ethereal diazomethane.

Saponification with 5% methanolic KOH (1 hr, steam bath) and crystallization from light petroleum gave the keto-carboxylic acid, m.p. 154–155° (Found: C, 71·42; H, 9·12. $C_{15}H_{24}O_3$ requires: C, 71·39; H, 9·59%). IR bands at: 3205 and 2625 (broad), 1709, 1692, 1295, 1247, 1190, 1155, 1124, 1031, 982, 925, 865 and 834 cm^{-1}.

Diol (XVI) *from hydroxyvalerananone* (I). To a solution of methyl lithium (prepared from 1·8 g Li and excess methyl iodide) in dry ether (50 ml) was added hydroxyvaleranone (1,440 mg) in dry ether (50 ml) and the mixture refluxed for 18 hr. The product, after usual working up, afforded the diol (425 mg), crystallized from light petroleum, m.p. 144–145° (Found: C, 75·82; H, 12·33. $C_{16}H_{30}O_2$ requires: C, 75·53; H, 11·89%). IR bands at: 3390, 1370, 1323, 1190, 1131, 1105, 1048, 1033, 1009, 980, 950, 927, 909, 884 and 832 cm^{-1}.

Alcohol (XVIII) *from diol* (XVI). The above diol (400 mg) was acetylated using pyridine (5 ml) and acetic anhydride (2 ml). After standing overnight, the diol monoacetate was isolated in the conventional manner. IR spectrum showed the presence of hydroxyl (3571 cm^{-1}) and acetoxy functions (1727, 1250 cm^{-1}).

The above acetate in acetic acid (20 ml) and *p*-toluenesulphonic acid monohydrate (50 mg) was heated under reflux for 25 min and cooled. After usual processing, the unsaturated acetate (XVII, 316 mg) was obtained. IR bands at: 1733, 1374, 1362, 1242, 1031, 990, 970 and 804 cm^{-1}.

Saponification of the above acetate with 5% methanolic KOH (30 min, steam bath) and usual working up gave the alcohol (XVIII, 248 mg), b.p. 150–160° (bath)/0·5 mm. (Found: C, 81·83; H, 12·32. $C_{16}H_{28}O$ requires: C, 81·29; H, 12·32%). IR bands at: 3436, 1377, 1366, 1098, 1058, 1024, 1010, 985, 930, 918 and 804 cm^{-1}.

Eudalene (XX) *from alcohol* (XVIII). To a solution of the unsaturated alcohol (150 mg) in acetone (10 ml) excess Jones reagent was added and the mixture left at room temp. for 30 min. After this period, a few drops of methanol were added and the mixture diluted with a large excess water. Extraction with ether and separation of acidic and neutral portions in the usual manner gave the acid (XIX, 80 mg). The crude acid was heated with Se (80 mg) at 300° for 6 hr. The product was extracted with ether, the ether removed and the oily residue filtered through alumina. The yellow oil (14 mg) contained 60% naphthalenic material. The identity with eudalene was established by mixed VPC analysis on two stationary phases.

Isolation of acetyl hydroxyvaleranone (XIV.) This was isolated from the fraction N_3 of Indian valerian root oil.[1] The chromatographic fractions which were eluted earlier than hydroxyvaleranone showed the presence of acetoxy and ketonic carbonyl functions (*vide infra*). The crude fraction (3 g) was treated with semicarbazide hydrochloride and sodium acetate and the semicarbazone obtained in the manner described for isolation of hydroxy-valeranone. Repeated crystallizations from ethanol afforded pure semicarbazone, m.p. 180–181° (Found: N, 12·23. $C_{18}H_{31}O_3N_3$ requires N, 12·45%).

Regeneration of the parent compound by oxalic acid–light petroleum procedure yielded acetyl hydroxy-valeranone, b.p. 180–185° (bath)/0·3 mm, $(\alpha)_D$ −54·0° (*c*, 4·0). The IR spectrum was identical with the acetyl derivative prepared from hydroxy valeranone.

Hydrolysis of the keto-acetate with 5% methanolic KOH for 1 hr (steam bath) gave hydroxy-valeranone m.p. and mixed m.p. 53°.