Carbowax 20 M column was used with the same GC conditions as described above.

IR. Obtained on thin films on ultra-micro demountable NaCl plates in a spectrometer fitted with a beam condenser.

Quantitative analysis. The percentage composition of components in the essential oil (Table 1) was based on the area percentage of each component on the GC trace measured by electronic integration.

Acknowledgements—We thank Dr. W. M. Longhurst and Dr. J. M. Tucker for authentication of the tree used in this study.

REFERENCES

1. Longhurst, W. M., Oh, H. K., Jones, M. B. and Kepner, R. E. (1968) *Trans. North Am. Wildl. Nat. Resour. Conf.* **33**, 181.
2. Steinhagen, E., Abrahamsson, S. and McLafferty, F. W. (1974) *Registry of Mass Spectral Data.* John Wiley, New York.
3. (1973) *Sadtler Standard Infrared Spectra.* Sadtler Research Laboratories, Philadelphia.
4. von Sydow, E., Anjou, K. and Karlsson, G. (1970) *Mass Spectra Data of Terpenes*, SIK-Rapport, No. 279.
5. Oh, H. K., Sakai, T., Jones, W. B. and Longhurst, W. M. (1967) *Appl. Microbiol.* **15**, 777.
6. Okamoto, R. A., Ellison, B. O. and Kepner, R. E. (1981) *J. Agric. Food Chem.* **29**, 324.

Phytochemistry, Vol. 22, No. 6, pp. 1505–1506, 1983.
Printed in Great Britain.

0031–9422/83/061505–02$03.00/0

A STRUCTURE OF FAURINONE, A SESQUITERPENE KETONE ISOLATED FROM *VALERIANA OFFICINALIS**

R. Bos, H. Hendriks, J. Kloosterman† and G. Sipma†

Laboratory of Pharmacognosy, State University of Groningen, Ant. Deusinglaan 2, NL-9713 AW Groningen, The Netherlands; †Research Laboratory, P.F.W. (Nederland) B.V., P.O. Box 3, NL-3800 AA Amersfoort, The Netherlands

(*Received* 7 *September* 1982)

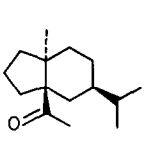
Key Word Index—*Valeriana officinalis*; Valerianaceae; sesquiterpenoid; faurinone; IR; ^{1}H NMR; ^{13}C NMR; mass spectrometry.

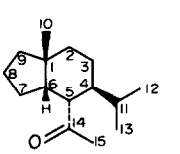
Abstract—A sesquiterpenoid, $C_{15}H_{26}O$, was isolated from *Valeriana officinalis* of which the spectral data (IR, NMR and mass spectra) were in agreement with those of faurinone. Based on ^{13}C NMR, and ^{13}C and ^{1}H NMR shift and decoupling experiments a new structure for faurinone is proposed.

From the sesquiterpene part of the essential oil of *Valeriana officinalis* L. s. l., we isolated, by prep. GC and TLC a ketone, $C_{15}H_{26}O$, of which the spectral characteristics, IR, NMR and mass spectra, were identical with those of faurinone (**1**), first reported by Hikino *et al.* [1]. A ^{13}C NMR spectrum of this compound revealed the presence of only one quaternary carbon atom, which was not in accordance with the proposed structure **1** [2].

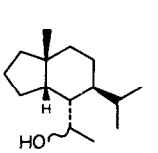
Based on extensive ^{1}H and ^{13}C NMR shift and decoupling experiments, we propose structure **2** for faurinone. Addition of the shift reagent Eu(fod)$_3$ to a solution of faurinone results in the separation of the NMR signals of the methyl group of the acetyl group, H-5 and H-4, all originally positioned around δ 2.2. The relative shifts of these protons are: H-5, 119 and H-4, 90, based on 100 for the methyl of the acetyl group. The H-5 is a double doublet, (J = 10.4 and 4.8 Hz) and is coupled to H-4 (J = 10.4 Hz), which is a double triplet (J = 10.4 and 3.8 Hz). The second proton to which H-5 is coupled is H-6 (J = 4.8 Hz). Correlation with the ^{13}C NMR spectrum by selective decoupling experiments showed that H-4–H-6 are all doublets and, thus, all CH-groups. Another proton showing a large relative shift (97) is the CH of the isopropyl group. The relative shift of one of the methyl groups of the isopropyl group is 66, compared to a relative shift of 24 for the second methyl group of the isopropyl group.

This information together with the results of the selective ^{13}C NMR decoupling experiments and other ^{1}H NMR decoupling experiments with different Eu(fod)$_3$ concentrations leads us to structure **2** for faurinone, the configuration with an equatorial acetyl and an equatorial isopropyl group. Hikino *et al.* [2] based the position of the





2



3

*Part of this study was presented at the 12th International Workshop on Essential Oils, Marburg, West Germany, 1981, as a poster.

acetyl group in structure **1** mainly on the fact that only three protons were exchanged by deuteration under basic conditions (2 N NaOD in D_2O), but the exchange of protons of the nucleus, dependent on the configuration, can be much hindered or take place only under very severe conditions [3, 4]. Reduction of faurinone with lithium aluminium hydride gives two isomeric alcohols, of which the NMR spectra are in agreement with structure **3**.

EXPERIMENTAL

Distillation of the essential oil. Dry roots of *Valeriana officinalis* L. s.l. (VNK) were submitted to steam distillation following the method of Hendriks [5] and yielded 0.55% (w/v) essential oil.

Isolation of faurinone. 1 g essential oil was divided into several fractions by CC on Si gel (1 m × 4 cm; Merck Kieselgel 60, 70–230 mesh) using petrol (bp < 40°) containing an increasing percentage of Et_2O (0–100%). The fraction eluted with 2% Et_2O (115 mg) contained valeranone (55.6%), valerenal (20.0%), a number of valerenyl esters* (9.6%) and faurinone (10.4%). Faurinone was isolated by prep. GC, using a 2 m stainless steel column (i.d. 2.3 mm) with 10% Carbowax 20 M on Chromosorb G-HP, 80–100 mesh, temp. 80–200°, temp. programming 4°/min, flow 30 ml N_2/min.

Synthesis of the faurinols. 110 mg faurinone in 0.5 ml dry Et_2O was added to 10 mg $LiAlH_4$ in 1 ml dry Et_2O. After 10 min a few drops of EtOAc and 5 ml H_2O were added to this soln, which was poured into 10 ml 2% H_2SO_4. After extraction with Et_2O (3 × 10 ml) and drying with Na_2SO_4, 73 mg of faurinol isomers was obtained.

Isolation of the faurinol isomers. The two isomers were separated by prep. TLC, using Schleicher and Schüll prep. TLC plates (Si gel G 1510/LS 254, 1 mm) with a mobile phase of petrol–Et_2O (7:3).

Faurinone (**2**). ^{1}H NMR and MS data are in agreement with the data in ref. [2]. IR ν_{max}^{film} cm^{-1}: 1710 (C=O), 1454, 1366, 1353, 1295, 1289, 1268, 1231, 1191, 1172, 1154, 1083, 1052, 1030, 984, 958, 918, 895, 878, 862, 843, 821, 795, 772, 581, 469; ^{13}C NMR (25 MHz, $CDCl_3$, TMS as int. standard): δ 211.8 (*s*, C-14), 50.9 (*d*, C-6), 49.3 (*d*, C-5), 47.3 (*d*, C-4), 41.6 (*s*, C-1), 36.6 (*q*, C-10), 32.4 (*t*), 30.8 (*t*), 29.2 (*q*, C-15), 29.0 (*d*, C-11), 26.5 (*t*), 23.0 (*q*, C-13), 22.2 (*q*, C-12), 21.4 (*t*).

Faurinol-1 (*one isomer of structure* **3**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3625 and 3500 (OH), 1470, 1460, 1385, 1370, 1310, 1240, 1168, 1129, 1115, 1089, 1037, 1024, 996, 964, 939, 911, 893, 877, 618; ^{1}H NMR (99.55 MHz, $CDCl_3$, TMS as int. standard): δ 4.06 (1H, *br q*, *J* = 6.4 Hz, H-14), 1.17 (3H, *d*, *J* = 6.3 Hz, Me-15), 1.04 (3H, *s*, Me-10), 0.99 (3H, *d*, *J* = 6.1 Hz, Me-12), 0.87 (3H, *d*, *J* = 6.1 Hz, Me-13); ^{13}C NMR (25 MHz, $CDCl_3$, TMS as int. standard): δ 68.0 (*d*, C-14), 52.4 (*d*, C-4), 46.8 (*d*, C-6), 42.2 (*s*, C-1), 40.3 (*d*, C-5), 37.7 (*t*), 34.0 (*t*), 33.5 (*q*, C-10), 29.1 (*d*, C-11), 27.3 (*t*), 23.7 (*q*, C-13), 22.7 (*q*, C-12), 22.6 (*t*), 21.8 (*q*, C-15), 20.6 (*t*); MS 70 eV *m/z* (rel. int.): 206 (35), 191 (15), 180 (17), 179 (24), 165 (15), 163 (67), 137 (13), 135 (19), 123 (100), 121 (17), 109 (35), 107 (15), 97 (11), 96 (11), 95 (45), 93 (13), 83 (19), 81 (35), 69 (22), 67 (13), 55 (13), 43 (19), 41 (13).

Faurinol-2 (*the other isomer of structure* **3**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3625 and 3460 (OH), 1470, 1460, 1378, 1247, 1170, 1108, 1089, 1066, 1053, 1027, 960, 942, 910, 891, 873, 636, 608; ^{1}H NMR (99.55 MHz, $CDCl_3$, TMS as int. standard): δ 4.13 (1 H, *dq*, *J* = 6.1 and 2.8 Hz, H-14), 1.13 (3H, *d*, *J* = 6.3 Hz, Me-15), 1.02 (3H, *s*, Me-10), 0.88 (3H, *d*, *J* = 5.8 Hz, Me-12), 0.87 (3H, *d*, *J* = 5.8 Hz, Me-13); ^{13}C NMR (25 MHz, $CDCl_3$, TMS as int. standard): δ 69.0 (*d*, C-14), 52.4 (*d*, C-4), 47.7 (*d*, C-6), 42.3 (*s*, C-1), 41.4 (*d*, C-5), 37.8 (*t*), 34.3 (*t*), 33.6 (*q*, C-10), 29.2 (*d*, C-11), 27.4 (*t*), 23.5 (*q*, C-12, C-13), 22.7 (*t*), 20.3 (*t*), 17.8 (*q*, C-15); MS 70 eV *m/z* (rel. int.): 206 (24), 191 (9), 179 (9), 165 (7), 163 (60), 137 (10), 135 (15), 123 (100), 121 (11), 109 (27), 97 (8), 96 (8), 95 (34), 83 (14), 81 (27), 69 (13), 67 (10), 55 (9), 43 (8).

*Poster presented at the 13th International Workshop on Essential Oils. Würzburg, West Germany, 1982.

REFERENCES

1. Hikino, H., Hikino, Y., Takeshita, Y., Kato, H. and Takemoto, T. (1965) *Yakugaku Zasshi* **85**, 179.
2. Hikino, H., Hikino, Y., Agatsuma, K. and Takemoto, T. (1968) *Chem. Pharm. Bull.* **16**, 1779.
3. Thomas, A. F. and Willhalm, B. (1965) *Tetrahedron Letters* **18**, 1309.
4. Williams, D. H., Wilson, J. M., Budzikiewicz, H. and Djerassi, C. (1963) *J. Am. Chem. Soc.* **85**, 2091.
5. Hendriks, H. (1973) *Planta Med.* **24**, 158.