Fraxidin 8-O-β-D-glucoside tetraacetate (**5**). Acetylation of (**4**) (50 mg), gave a colourless syrup (80 mg). The compound was purified by chromatography (Et_2O–EtOAc, 85:15), followed by passing a CH_2Cl_2-soln through charcoal and thorough drying; $[\alpha]_D^{22}$ −37° (*c* 0·4 in EtOH); UV-spectrum: λ_{max}^{EtOH} 230 nm (ε 17·800), 294 nm (ε 8·300), and 343 nm (ε 6·500). ^1H NMR spectrum: 7·60 and 6·33 ppm (*d*'*s*; $J_{2,3}$ 9·5 Hz, H-4 and H-3), 6·73 ppm (*s*; H-5), 5·50–5·10 ppm (*m*; H-1′, H-2′, H-3′, H-4′), 4·21 and 4·13 ppm, (*dd*'*s*; H-6′ and H-6″), 3·95 and 3·89 ppm (*s*'*s*; 2 × OMe), 3·75 ppm (*m*; H-5′), 2·11 and 2·00 ppm (1 and 3 OAc). Found: C, 54·15; H, 5·34, $C_{25}H_{28}O_{14}$ requires: C, 54·36; H, 5·11%.

Acknowledgements—We thank Dr. M. Terazawa, Obihiro Zootechnical University, Japan, for useful information and for a sample of mandshurin tetraacetate, Dr. Kamikawa, Osaka City University, Japan, for spectra of ligstroside derivatives, and Prof. A. Kjær of this Institute for help with the manuscript.

REFERENCES

1. Hegnauer, R. (1969) *Chemotaxonomie der Pflanzen* Vol. 5, 237. Birkhaüser Verlag, Basel.
2. Wessely, F. and Demmer, E. (1928) *Chem. Ber.* **61**, 1279;
3. Wessely, F. and Demmer, E. (1929) *Chem. Ber.* **62**, 120.
4. Späth, E. and Jerzmanowska-Sienkiewiczowa, Z. (1937) *Chem. Ber.* **70**, 698, 1019.
5. Janot, M.-M., Le Men, J., Pourrat, H. and Plouvier, V. (1955) *Bull. Soc. Chim. Biol.* **37**, 365.
6. Plouvier, V. (1968) *Compt. Rend.* **266D**, 1526.
7. Terazawa, M. and Sasaya, T. (1970) *J. Japan Wood Res. Soc.* **16**, 192.
8. Bock, K., Jensen, S. R. and Nielsen, B. J. *To be published.*
9. Asaka, Y., Kamikawa, T., Kubota, T. and Sakamota, H. (1972) *Chemistry Letters* 141.
10. Inouye, H., Yoshida, T., Tobita, S., Tanaka, T. and Nishioka, T. (1974) *Tetrahedron* **30**, 201.
11. Jensen, S. R., Nielsen, B. J. and Dahlgren, R. (1975) *Botaniska Notiser* (*Lund*) **128**, 119.
12. Inouye, H., Nishioka, T. and Kaniwa, M. (1975) *Phytochemistry* **14**, 304.
13. Terazawa, M., Obihiro Zootechnical University, Japan. Private communication.
14. Kubota, T., Ichikawa, N. and Kamikawa, T. (1968) *Nippon Kagaku Zasshi* **89**, 62.
15. Inouye, H. and Nishioka, T. (1972) *Tetrahedron* **28**, 4231.
16. Panizzi, L., Scarpati, M. L. and Oriente, G. (1960) *Gazz. Chim. Ital.* **90**, 1449.

Phytochemistry, 1976, Vol. 15, pp. 223–224. Pergamon Press. Printed in England.

NORCAPILLENE, A NEW ACETYLENIC HYDROCARBON FROM THE ESSENTIAL OIL OF *ARTEMISIA CAPILLARIS**

MITSUO MIYAZAWA and HIROMU KAMEOKA

Department of Applied Chemistry, Faculty of Science and Engineering,
Kinki University, Kowakae, Higashiosaka-shi, Osaka, Japan

(*Received* 13 *June* 1975)

Key Word Index—*Artemisia capillaris*; Compositae; essential oil; acetylenic hydrocarbon; norcapillene.

In previous papers [1, 2], the structures of the new acetylenic compounds, 1-(2′-methoxyphenyl)-2,4-hexadiyne (*o*-methoxycapillene) and capillanol in the essential oil of *Artemisia capillaris* Thunb. have been described. We now report a new acetylenic hydrocarbon, norcapillene.

The compound constitutes *ca* 0·1% of the essential oil and was isolated by preparative GLC, using Celite 545 as the stationary phase. The compound analysed for $C_{11}H_8$, n_D^{25} 1·6364. IR spectrum shows $-C\equiv C-$ str at 2220 and 2240 cm^{-1} (W), aromatic str at 1595 and 1490 cm^{-1} (M), aromatic adjacent 5H drf at 755 and 690 cm^{-1} (S). These data indicate that the compound is a aromatic monosubstituted hydrocarbon, with a C_5H_3 unit, whose structure $Ph(C\equiv C)_2Me$ (**1**) was elucidated from the NMR spectrum. This shows signals for 3 protons of methyl group in the α-position of the diacetylene bond at $\delta_{ppm}^{CCl_4}$ 1·98, as a singlet. The 5 protons in the benzene ring appeared as a broad singlet from δ 7·05 to 7·55. Consequently, the splitting pattern of the signals in the NMR spectrum appears to be in conformity with **1** for norcapillene. It had a UV spectrum almost superimposable with that of synthetic 1-phenyl-1,3-pentadiyne [3–6]. The formation of this phenylacetylene had been reported by H. Taniguchi *et al.* when 1-phenyl-1,4-pentadiyne and KOH in ethanol were kept under N_2 at *ca* 0° for 3 hr. The MS spectrum was also compatible with this structure. Besides the molecular ion peak at *m/e* 140 (98·2%) the other significant peaks discernible were at *m/e* 139 (M^+-H, 100·0%), 138 (M^+-H_2, 13·5%), 114 ($(\phi-C\equiv C-C\equiv CH)^+$, 29·8%), 113 ($\phi-C\equiv C-\dot{C}\equiv C^+$, 11·5%), 89 (7·2%), 88 (7·3%), 87 (10·1%), 63 (13·7%). Norcapillene was catalytically hydrogenated over PtO_2 in ethanol to give octahydronorcapillene, which was found to be identical with amylbenzene in all respects (IR, NMR, MS spectrum).

EXPERIMENTAL

Plant material and oil removal. A. capillaris was harvested in the suburbs of Osaka-Fu in October 1973. After steam distillation of 11·0 kg of the stalks and leaves, 88·3 g (0·803%) of the essential oil was obtained by the extraction of the distillate with Et_2O and by the evaporation of the solvent under N_2.

Isolation of norcapillene. Ten g of the essential oil was chromatographed on activated alumina (60 g, 300 mesh, a glass tube of *d* = 1·8 and 1 = 50 cm) with *n*-hexane to elute the terpene hydrocarbons. Subsequent elution with C_6H_6 gave norcapillene which was then isolated by prep. GLC (Carbowax-20 M 5%, 80–100 mesh, 4 mm 3·00 m, He 0·5 kg/cm^2).

---

* Presented at the 18th Symposium on Chemistry of Terpenes, Essential Oil and Aromatics, of Japan, Chiba, 1974.

Spectroscopy. NMR spectra were determined at 60 MHz, in CCl_4 and with trimethylsilane as internal standard; values are given in ppm (δ) relative to trimethylsilane.

Catalytic hydrogenation of the norcapillene. Catalytic hydrogenation of the norcapillene (55 mg) in EtOH (5 ml) over PtO_2 (1·5 mg) was carried out at room temp. for 2·5 hr. The product was purified by preparative TLC (kieselgel GF254) using *n*-hexane C_6H_6 (2:1), as was obtained as a colorless oil. NMR: $\delta^{CCl_4}_{ppm}$ 0·88 (3H, *t*, CH_2–$C\underline{H}_3$), 1·26 (6H, *m*, –$(C\underline{H}_2)_3$–), 2·68 (2H, *t*, ϕ–$C\underline{H}_2$–), 7·23 (5H, *m*, ϕ–). (Found: C, 89·11%; H, 10·89%. Calcd for $C_{11}H_{16}$: C, 89·12%; H, 10·88%).

REFERENCES

1. Miyazawa, M. and Kameoka, H. (1975) *Phytochemistry* **14**, 1126.
2. Miyazawa, M. and Kameoka, H. (1975) *Phytochemistry* **14**, 1126.
3. Quang, L. V. and Cadiot, P. (1965) *Bull. Soc. Chem. France* 1525.
4. Taniguchi, H., Mathai, I. M. and Miller, S. I. (1966) *Tetrahedron* **22**, 867.
5. Quang, Y. V., Quang, L. V. and Emptoz, G. (1964) *Compt. Rend.* **258**, 4586.
6. Migniac, L. G. (1961) *Ann. Chim.* **6**, 1071.

Phytochemistry, 1976, Vol. 15, p. 224. Pergamon Press. Printed in England.

NORSEYCHELANONE, α- AND β-PATCHOULENES AND PATCHOULI ALCOHOL FROM *NARDOSTACHYS JATAMANSI*

G. Rücker*, J. Tautges*, M. L. Maheswari† and D. B. Saxena†

* Institut für Pharmazeutische Chemie der Westfälischen Wilhelms-Universität Münster, BRD;
†Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi 110012, India

(*Received* 24 *June* 1975)

Key Word Index—*Nardostachys jatamansi*; Valerianaceae; norseychelanone; α- and β-patchoulenes; patchouli alcohol.

Plant Nardostachys jatamansi DC, Valerianaceae. *Origin*: India, from the Himalaya mountains at a height of 3000–5000 m. The plant purchased from the local market. *Previous work* on the roots [1–3].

Isolation 24 kg air-dried roots are exhaustively extracted with light petrol (35–40°). Solvent was evaporated *in vacuo* and the residue (900g) extracted with Na_2CO_3-solution. The insoluble portion was chromatographed on a silica gel column (180 × 2·0 cm) using light petroleum (60°)–EtOAc, 8:2 as eluent. The fraction with R_f 0·78 (TLC same solvent) was found to be norseychelanone isolated for the first time from any plant source. The fraction R_f 0·70, formed colourless crystals mp 55–56° (patchouli alcohol). The fractions having R_f 0·90–1·0 were rechromatographed on silica gel columns impregnated with 10% $AgNO_3$, using hexane as an eluent. TLC showed spots at R_f 0·5, 0·60, 0·68 and 0·80. The bright red spot (R_f 0·45) was identified as seychellen [4,5], confirmed by IR, NMR and MS.

Identification Norseychelanone: Identical with the compound obtained by degradation of seychellen, TLC, IR, NMR, MS [4,5]. *Patchouli alcohol*: IR [6–9], MS [7–9], TLC (Kieselgel Merck PF_{254}), Anisaldehyde–H_2SO_4: carmine red, R_f: 0·70. *α- and β-Patchoulenes*: by GC–MS (Varian-CH7), 3·8% SE 30, 100°C/6° 2 min to 250°. The GLC of the mixture showed 4 peaks having R_t: 5,3/9,15/10, 0 and 11, 0 min. For further identification by GLC 50% reference substances were added to the mixture. β-Patchoulene showed an increase in the height of the peak with R_t 9,15 min. MS: m/e(%) 204(60M^+), 189(98), 161(100), 156(30), 135(30), 133(40), 119(70), 105(60), 93(50), 91(50), 79(30), 77(25). α-Patchoulene showed an increase in the height of the peak R_t 11·0 min. MS: m/e(%) 204(20M^+), 189(20), 161(30), 135(80), 119(45), 108(50), 107(90), 105(55), 93(100), 91(50), 81(20), 79(30), 77(30), 55(50).

Acknowledgements—We thank Dr. Bruhn and Dr. Klein, DRAGOCO Co., Holzminden, BRD, for supplying the spectra and reference substances.

REFERENCES

1. Rücker, G. and Glauch, G. (1967) *Deut. Apotheker-Z.* **27**, 921.
2. Sastry, S. D., Maheswari, M. L., Chakravarti, K. K. and Bhattacharyya, S. C. (1967) *Ess. Oil Record* **58**, 154.
3. Rücker, G. and Tautges, J. (1974) *Arch. Pharmaz.* **307**, 791.
4. Wolf, G. and Ourisson, G. (1969) *Tetrahedron* **25**, 4903.
5. Maheswari, M. L. and Saxena, D. B. (1974) *Ind. J. Chem.* **12**, 1221.
6. Büchi, G. and Erickson, R. N. (1956) *J. Am. Chem. Soc.* **78**, 1262.
7. Yamaguchi, K. (1970) *Spectral Data of Natural Products* Vol. 1. Elsevier, Amsterdam.
8. Hill, H. C., Reed, J. R. and Robert-Lopes, M. T. (1968) *J. Chem. Soc. C* (*London*) p. 93.
9. Dobler, M., Dunitz, J. D., Gubler, B., Weber, H. P., Büchi, G. and Padilla, J. (1963) *Proc. Chem. Soc.* (*London*) p. 383.