Phytochemistry, Vol. 21, No. 12, pp. 2981–2982, 1982.
Printed in Great Britain.

0031-9422/82/122981-02$03.00/0
Pergamon Press Ltd.

TERPENES FROM PITTOSPORACEAE

ESTHER K. NEMETHY and MELVIN CALVIN

Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, CA 94720, U.S.A.

(*Received* 10 *March* 1982)

Key Word Index—*Pittosporum resiniferum*; *P. undulatum*; Pittosporaceae; essential oil; monoterpenes; α-pinene; myrcene; limonene.

Abstract—The monoterpenes of the fruits of *Pittosporum resiniferum* and *P. undulatum* have been identified. The essential oil of *P. resiniferum* contains myrcene and α-pinene in equal quantities, whereas the major terpene of *P. undulatum* oil is limonene.

The fruits of the tree *Pittosporum resiniferum* (Pittosporaceae) have been reported to contain the unusual natural product *n*-heptane [Fernandez, E., personal communication]. It is reported that even the green fresh fruit will burn brilliantly when a match is applied to it and that the expressed oil of the fruit is flammable. This species is native to the Philippines where the nuts are sometimes used as torch light [1]. *Pittosporum* fruit, therefore, shows promise as a potential alternate liquid energy source, and we have examined the chemical composition of this oil. The two alkanes *n*-heptane and *n*-nonane are minor components of this oil; the major components are two volatile monoterpenes, α-pinene and myrcene.

Another species of the family, *P. undulatum*, is widespread in California, and it produces small fragrant orange fruits in abundance. These fruits were collected on the University of California Berkeley campus during November and December 1981. No *n*-alkanes could be detected in the oil of *P. undulatum*. Limonene is the only major monoterpene present in this oil, accounting for 99% of the monoterpene fraction; α-pinene is a minor component. No oxygenated monoterpenes were detected in either of the oils, but both contained minor quantities of sesquiterpene hydrocarbons.

A few members of the Pittosporaceae have been subject to phytochemical investigation. Phytosterols have been isolated from the bark of *P. floribundum* [2], *P. colensoi* and *P. eugenoides* [3]. Polyacetylenes have been isolated from roots of *P. buchanani* [4], *P. crassifolium*, *P. tobira* and *P. undulatum* [5]. However, there are no prior reports on the essential oils of any *Pittosporum* species.

EXPERIMENTAL

Capillary GC analyses were obtained using either a 40 m SP2250 SCOT or an 80 m Carbowax 20 M column, temp. programmed from 40 to 200° at 4°/min. Where indicated, percentages refer to computer-calculated peak areas without correction to response. Preparatory GC was carried out on a 10 feet × 4 mm i.d. 10% SP2250 glass column at 110°. Coupled GC/MS was carried out on the SP2250 column interfaced to a Finnigan 4000 mass spectrometer at 70 eV. ^{1}H NMR spectra were recorded at 250 MHz in $CDCl_3$ with TMS as int. standard.

Analysis of P. resiniferum *essential oil.* Ripe fruits were homogenized, then extracted with CH_2Cl_2 by stirring under N_2 at ambient temp. for 24 hr. After slow distillation of the CH_2Cl_2 a light orange oil, 8–10% of the fr. wt was obtained. GC/MS analysis of the oil indicated the presence of *n*-heptane (5%),* *n*-nonane (7%), three isomeric monoterpenes (85%) and six minor sesquiterpenes (6%). The two major monoterpenes were isolated by prep. GC and identified as α-pinene (38%) and myrcene (40%) by ^{1}H NMR, MS and coelution with standards on the SP2250 and Carbowax 20M capillary columns. Catalytic hydrogenation of the oil (Pd on C, 1 atm.) gave pinane and 2,6-dimethyl-octane, identified by MS and GC retention time. *α-Pinene.* ^{1}H NMR (250 MHz) δ 5.17 (1H, *s*), 2.33 (1H, *m*), 2.2 (2H, *br s*), 2.18 (1H, *br s*), 1.94 (1H, *m*), 1.65 (3H, *s*), 1.26 (3H, *s*), 1.5 (2H, *m*), 0.83 (3H, *s*). MS (*m/z*): 136, 121, 107, 105, 93 (bp), 79, 77. *Myrcene*: ^{1}H NMR (250 MHz) δ 6.37 (1H, *m*; $J = 10.7$, 17.6 Hz), 5.4–4.9 (5H), 2.2 (4H, *m*), 1.7 (3H, *s*), 1.6 (3H, *s*). MS (*m/z*): 136, 121, 107, 94, 93 (bp), 69, 41.

Analysis of P. undulatum *essential oil.* Fr. fruits were extracted in the same manner as before, but with light petrol. A light orange oil, 4–5% of the fr. fruit wt, was obtained. Chromatography on Si gel, eluting with petrol, gave the hydrocarbon fraction which was 50% of the oil. GC and GC/MS analyses showed the presence of two monoterpenes in a ratio of 10:1, which coeluted with limonene and α-pinene, respectively. Limonene was purified by prep. GC and identified by ^{1}H NMR. Catalytic hydrogenation of the oil (Pd on C, 1 atm.) gave 1-isopropyl-4-methylcyclohexane and pinane, identified by MS and GC retention times. *Limonene*: ^{1}H NMR (250 MHz) δ 5.7 (1H, *s*), 4.7 (2H, *s*), 2.2–1.67 (5H, *m*), 1.67 (3H, *s*), 1.59 (3H, *s*), 1.47–1.4 (2H, *m*). MS (*m/z*): 136, 121, 107, 93, 79, 68 (bp).

Acknowledgements—We thank R. Hurov for the supply of *Pittosporum resiniferum* nuts. This work was supported by the Assistant Secretary for Conservation and Solar Energy, Office of Solar Applications for Industry, Department of Energy under Contract No. W-7405-ENG-48.

---

*The percentage of *n*-heptane may be too low, since some may have evaporated in transit.

REFERENCES

1. Noble, B. (1978) *Canopy* **4**, 4.
2. Desai, H. K., Gawad, D. H., Joshi, B. S., Parthasarathy, P. D., Ravindranath, K. R., Saindane, M. T., Sidhaye, A. K. and Viswanathan, N. (1976) *Ind. J. Chem.* **15**, 291.
3. Cambrie, R. and Parnell, J. C. (1969) *N. Z. J. Sci.* **12**, 453.
4. Bohlmann, F. and Rode, K. (1968) *Chem. Ber.* **101**, 1889.
5. Bohlmann, F. and Zdero, C. (1975) *Chem. Ber.* **108**, 2541.

Phytochemistry, Vol. 21, No. 12, pp. 2982–2984, 1982.
Printed in Great Britain.

0031-9422/82/122982-03$03.00/0

NEW CADINENE DERIVATIVES FROM *HETEROTHECA LATIFOLIA**

FERDINAND BOHLMANN, RAJINDER K. GUPTA, ROBERT M. KING† and HAROLD ROBINSON†

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany;
†Smithsonian Institution, Washington, DC 20560, U.S.A.

(*Received* 18 *November* 1981)

Key Word Index—*Heterotheca latifolia*; Compositae; Astereae; sesquiterpenes; cadinene derivatives.

Abstract—*Heterotheca latifolia* afforded several new acids all derived from cadinane.

So far five species of the North American genus *Heterotheca* have been investigated chemically [1–3]; however, in only three species have the aerial parts been investigated. The roots of *H. latifolia* Buckl. gave a C_{10}-acetylenic compound which is widespread in the tribe [2]. We have now studied the aerial parts of *H. latifolia*. In addition to germacrene D, caryophyllene and bicyclogermacrene several cadinene derivatives were present, the already known angelate **1** [3] and the acids **2a**–**9a**, which could be separated only after esterification with CH_2N_2. The main compound was the acetate **2b**. Its ^1H NMR spectrum (Table 1) indicated the presence of an α,β-unsaturated ester group with a β-hydrogen (δ 7.33 *d*, $J = 2$ Hz) and an olefinic methyl group (δ 1.62 *s*, *br*). A broadened doublet at δ 2.72 was coupled with the olefinic proton and with the olefinic methyl indicating a similar situation as in **1**. The position of the acetoxy group followed from the chemical shift of the corresponding signal for the proton under the acetoxy group. As this signal showed small vicinal couplings only, a 2β-orientation was assumed, especially as a very similar 2α-alcohol [3] showed larger couplings ($J_{1,2} = 5.5$ Hz). Though some signals were overlapped, spin decoupling and $Eu(fod)_3$ induced shifts clearly supported the proposed structures. The esters **3b**–**5b** could not be separated. However, the ^1H NMR spectrum showed that they differed from **2b** only by the ester residues at C-2. The typical ester signals indicated the nature of these groups (Table 1). The ester **6b** was isomeric with **2b**. Spin decoupling showed that in this case the acetoxy group had to be placed at C-8. Again, a β-orientation was more likely though an α-position could not be excluded. The ^1H NMR data of **7b** (Table 1) showed the presence of a hydroxylated isopropyl group. One methyl doublet was replaced by two double doublets at δ 3.76 and 3.47. These were coupled with a multiplet at δ 2.15, which was also coupled with the remaining methyl doublet at δ 1.07. The other signals were close to those of **2b** indicating the same stereochemistry. Two further alcohols, were obviously isomeric at C-10 only. Both compounds, **8b** and **9b** afforded **10** after heating with *p*-toluenesulfonic acid in benzene. The relative configurations were assigned by the observed shift differences for H-10. In the spectrum of **9b** this signal was shifted downfield most probably due to the *cis*-orientated 7-hydroxy group.

The absolute configurations of the natural compounds could not be assigned with certainty, the given ones are the most probable from biogenetic considerations. The newly isolated cadinene derivatives provide further support that these compounds are characteristic for the genus *Heterotheca*.

---

*Part 347 in the series "Naturally Occurring Terpene Derivatives". For Part 346, see Bohlmann, F., Suwita, A., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20**, 1649.