Phytochemistry, 1973 Vol. 12, pp. 1405 to 1407. Pergamon Press. Printed in England.

ISOLATION AND THE STRUCTURE OF DEOXOPINGUISONE FROM THE LIVERWORT *PTILIDIUM CILIARE**

S. M. KRUTOV†, Z. SAMEK, V. BENEŠOVA and V. HEROUT

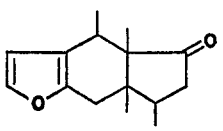
Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

(*Revised Received* 4 *December* 1972. *Accepted* 14 *December* 1972)

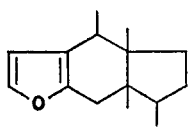
Key Word Index—*Ptilidium ciliare*; Bryophyta; liverwort; deoxopinguisone.

Abstract—A pure substance has been isolated from the liverwort *Ptilidium ciliare* of composition $C_{15}H_{22}O$. On the basis of the correlation of its IR and PMR spectra with those of pinguisone (I), it has been assigned structure of deoxopinguisone (II). This was confirmed by comparison with synthetic deoxopinguisone prepared from authentic pinguisone isolated from *Aneura pinguis*.

EXCEPT for lunularic acid,[1,2] which plays the role of an endogeneous growth inhibitor in liverworts, there are only a few cases where substances of the same type[3,4] have been found in several species of these plants. Some years ago, pinguisone[5] (I) was is olated as the



(I)



(II)

* Part CCXXV in the series "On terpenes". For Part CCXXIV see BENEŠOVÁ, V., SEDMERA, P., HEROUT, V. and ŠORM, F. (1973) *Colln. Czech. Chem. Commun.* in press.

† Visiting Scientist from Forest Technical Academy, Leningrad, U.S.S.R.

[1] PRYCE, R. J. (1971) *Planta* **97**, 354.
[2] HUNECK, S. and PRYCE, R. J. (1971) *Z. Naturforsch.* **26b**, 738.
[3] HUNECK, S. (1970) *Z. Naturforsch.* **25b**, 227; *idem.* (1971) *Acta Chem. Scand.* **25**, 1486.
[4] BENEŠOVÁ, V. SAMEK, Z., HEROUT, V. and ŠORM, F. (1969) *Colln. Czech. Chem. Commun.* **34**, 1807.
[5] BENEŠOVÁ, V., SAMEK, Z., HEROUT, V. and ŠORM, F. (1969) *Colln. Czech. Chem. Commun.* **34**, 582.

major component from the liverwort *Aneura pinguis* and we have now isolated a pure liquid from the related liverwort *Ptilidium ciliare*, which we have identified as deoxopinguisone (II).

The structure of the new substance as (II) follows both from the IR spectrum, which, except for the frequencies characteristic of a 3,4-di-substituted furan (1507, 1556, 1641, 3110 and 3140 cm^{-1}) did not contain any other peaks which could be assigned to other oxygen functions or other types of double bonds, and from the PMR spectrum, which displays characteristic signals of two protons of an α,β-disubstituted furan ring (6·19*d* and 7·24 ppm, $J_{\alpha,\beta}$ 2·0 Hz), two secondary methyl groups (δ 1·11 *d*, $J \approx 7{\cdot}0$ Hz and δ 0·85, $J \leq 6{\cdot}9$ Hz), and two tertiary methyl groups (δ 0·81 and 0·72).

The structure was confirmed by the synthesis of deoxopinguisone (II) by a modified Wolff–Kishner reduction[6] of authentic pinguisone (I). The identinty of the native and the synthetically prepared deoxopinguisone (II) was proved on the basis of the identity of their IR, MS and NMR spectra. Furthermore, deoxopinguisone (II) gave, on hydrogenation on palladium; two diastereomeric tetrahydro derivatives which were separated by chromatography on silica gel. Identical tetrahydrodeoxopinguisones were also prepared by a modified Wolff–Kishner reduction of two tetrahydro derivatives of pinguisone.[5]

EXPERIMENTAL

The IR spectra of the native and the synthetic deoxopinguisone (II) were measured as films using a Perkin–Elmer 621 apparatus; the spectra of other substances were measured in tetrachloromethane. The MS were measured on a AEI MS 902 spectrograph. The PMR spectra were measured in $CDCl_3$ on a Varian HA-100 apparatus, using TMS as internal standard. M.ps and b.ps were not corrected For column chromatography silica gel according to Pitra and Štěrba[7] was employed (30–60 μ), which was deactivated by the addition of 10% H_2O before use. For TLC, silica gel G Merck according to Stahl was used. R_fs were measured in the system *n*-heptane–EtOAc 7 3 unless stated otherwise.

Isolation of deoxopinguisone (II). *P ciliare* (360 g), collected in May in the neighbourhood of Soběslav in South Bohemia, was dried at normal temp., ground in a ball-mill, and the material obtained extracted with light petrol. The extracts (15 g) were concentrated and chromatographed on silica gel (100:1). Chromatography was monitored using TLC Deoxopinguisone (II) was eluted from the chromatographic column with light petrol. in the first fractions which were concentrated, and the residue distilled at 110–30° (bath temp.) and 8 mm Hg affording a colourless, non viscous liquid (0·20 g), which on TLC (detection with H_2SO_4–1% vanillin giving a brick-red spot of R_f 0·49; *n*-pentane). Pure deoxopinguisone (II) ,$C_{15}H_{22}O$ (M^+ 218; MS) is rather unstable in air and light, and changes rapidly to a brown–red viscous liquid.

Deoxopinguisone (II) *from pinguisone* (I) Freshly crystallized pinguisone[5] (I; 100 mg) was submitted to a modified Wolff–Kishner reduction.[6] The reaction product, isolated in the conventional manner, was purified by column chromatography on silica gel. The fractions obtained on elution with light petrol. gave a colourless, non-viscous liquid (15 mg; R_f 0 49, *n*-pentane) $C_{15}H_{22}O$ (M^+ 218; MS)

Tetrahydrodeoxopinguisones from deoxopinguisone (II). Deoxopinguisone (II; 9 mg) was hydrogenated in ethanolic solution on Pd/C The oily product was separated on a column of slicia gel to two liquid individual components, (3·9 mg; R_f 0·69) and (3 5 mg; R_f 0 62) Both diastereomeric tetrahydro derivatives had the composition $C_{15}H_{26}O$ (M^+ 222; MS).

Tetrahydropinguisones. A mixture of tetrahydropinguisones (30 mg), prepared on hydrogenation[5] of an authentic sample of pinguisone (I; 35 mg), was separated chromatographically to a crystalline diastereomer of mp 41–2°C (12 mg; R_f 0 53) and a liquid one of bp 120° (bath temp) (9 mg; R_f 0 49). Both tetrahydro derivatives had the composition $C_{15}H_{24}O_2$ (M^+ 236; MS)

Tetrahydrodeoxopinguisones from tetrahydropinguisones. Both diastereomeric tetrahydropinguisones (12 mg, R_f 0·53) and (9 mg; R_f 0·49) were reduced separately by the modified Wolff–Kishner method.[6] Two

diastereomeric deoxotetrahydropinguisones were obtained (1·8 mg; R_f 0·69 and 1·3 mg; R_f 0·62) the composition of which was $C_{15}H_{26}O$ (M^+ 222; MS).

Acknowledgements—For the identification of plant material our thanks are due to Dr. J. Váňa of the Department of Botany, Charles University, Prague. The mass spectra were measured and interpreted by Dr. L. Dolejš and the IR spectra were measured by Mrs V. Matoušková and interpreted by Dr. S. Vašíčková. We are grateful to all those mentioned as well as to Mrs B. Panáčková for technical assistance.

[6] BARTON, D. H. R., IVES, D. A. J. and THOMAS, B. R. (1955) *J. Chem. Soc.* 2056.
[7] PITRA, J. and ŠTĚRBA, J. (1962) *Chem. Listy* **56**, 544.