SHORT COMMUNICATION

CONSTITUENTS OF THE HYPERICUM ANDROSAEMUM

J. CARNDUFF, K. R. HARGREAVES and A. NECHVATAL

Queen's College and College of Technology, Dundee (Received 16 March 1966)

A STUDY of Hypericum androsaemum L. and Hypericum elatum Ait., two species of the Hypericum androsaemum (Keller's section), has shown the presence of α -terpineol and hydrocarbon waxes in the unripened seed capsules.

Hypericum androsaemum L.

The unripened seed capsules (10 kg) of tutsan (*H. androsaemum*)¹⁻³ were steam distilled, the ether extract of the distillate furnishing a pale yellow oil (3.5 ml) which on distillation yielded as a first fraction a colourless oil (0.6 ml), b.p. $62^{\circ}/0.5$ mm. An i.r. absorption spectrum and also a NMR spectrum of this oil ($[^{20}_{D}]^{\circ}] = -35.0$) proved to be identical with those spectra of an authentic specimen of (\pm) - α -terpineol. This oil was shown to contain 92 per cent α -terpineol by gas chromatography using an authentic sample as reference.

A third fraction (0·3 g), b.p. $115-120^{\circ}/0·5$ mm, solidified and was crystallized from ethanol to furnish a colourless solid, m.p. $38-42^{\circ}$, the i.r. spectrum of which showed it to be a straight-chain hydrocarbon. Gas chromatographic analysis of this solid showed the presence of the straight-chain hydrocarbons, $C_{19}H_{40}$, $C_{21}H_{44}$ and $C_{23}H_{48}$ in the ratio 3:5:2 respectively.

Hypericum elatum Ait.

The unripened seed capsules (10 kg) of H. elatum² were steam distilled, the ether extract of the distillate furnishing a pale yellow oil (2·0 ml) from which crystals separated. Fractional distillation of the filtrate yielded as a first fraction a colourless oil (0·4 ml), b.p. $62^{\circ}/0.5$ mm. In the same way as for tutsan berries (above), the oil was identified as α -terpineol (90 per cent pure).

The precipitate from the oil (see above) was sparingly washed with petroleum ether (b.p. $60-80^{\circ}$) to furnish colourless crystals (0·2 g), m.p. $52-54^{\circ}$. The i.r. absorption spectrum showed it to be a straight-chain hydrocarbon. Gas chromatographic analysis indicated the presence of the hydrocarbons $C_{27}H_{56}$ and $C_{29}H_{60}$ in the ratio 2:1 respectively as the main components of this solid. The second fraction, b.p. $125-130^{\circ}/0.5$ mm, of the oil distillate, solidified to a wax (0·4 g) which on crystallization from ethanol furnished a colourless crystalline solid, m.p. 59° . The i.r. absorption spectrum and gas chromatograph of this wax indicate that it is a mixture of straight-chain hydrocarbons, with $C_{27}H_{56}$ as the main component.

Acknowledgements—The authors gratefully acknowledge the help of the Shell Research Laboratories who performed the gas chromatography of the hydrocarbons cited above and also A. Boake Roberts & Co. who supplied an authentic sample of (\pm) - α -terpineol.

¹ K. R. HARGREAVES, Nature 206, 830 (1965).

² C. MATHIS and G. OURISSON, Phytochem. 3, 133; 3, 377 (1964).

³ R. SALGUES, Qualitas Plant. Mater. Vegitables 3, 38 (1961).