Identification of Pyrethrol with Taraxasterol

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The insecticidally inactive substance pyrethrol from pyrethrum flowers has been identified as taraxasterol.

THE OLEORESIN obtained by extraction of pyrethrum flowers (*Chrysanthemum cinerariaefolium* Vis.) contains not only the active insecticidal principles pyrethrin I and II,[1] but also comparatively large quantities of inactive material, including such compounds as the monocarbocyclic sesquiterpene lactone pyrethrosin (2) and an unidentified substance called "pyrethrol." The latter, first isolated by Fujitani (3) and referred to briefly by Staudinger and Ruzicka (4) had m.p. 199°, $[\alpha]_D$ + 73°, and was assigned (3) the molecular formula $C_{21}H_{34}O$. More recently (5), pyrethrol was stated to be a triterpene alcohol isomeric with lupeol.

The authors received a sample of crude pyrethrol[2] isolated a number of years ago (6) during the purification of pyrethrosin and have investigated its properties. Purification and conversion to a number of derivatives established its identity as taraxasterol.

In this laboratory, pyrethrol had m.p. 217–219° after several recrystallizations from chloroform–ethanol and $[\alpha]_D$ +92°.

The presence of 1 secondary hydroxyl group was indicated by the infrared and NMR spectra (complex signal at 3.2 p.p.m., H_3) and confirmed by the formation of a monoacetate, m.p. 246–248°, $[\alpha]_D$ +105°, NMR signal at 4.6 c (H_3), a monobenzoate, m.p. 244–247°, and by mild oxidation to a ketone, m.p. 179–182°, infrared band at 1710 cm.$^{-1}$, positive Zimmermann test, which contained no other hydroxyl groups. Furthermore, an exocyclic methylene group was clearly indicated in all four of the above compounds by infrared bands at 1650 and 890 cm.$^{-1}$ and, in the NMR spectra, by a broad singlet, $W_{1/2}$ 4 c/s, intensity 2 protons, at 4.65 p.p.m. The NMR spectra also indicated the presence of 7 methyl groups.

The melting points and rotations of pyrethrol and its derivatives bore a reasonable resemblance to those most widely accepted (7) for taraxasterol, m.p. 226–227°, $[\alpha]_D$ +97°; acetate, m.p. 256–257°, $[\alpha]_D$ +100°; benzoate, m.p. 242–244°; taraxastenone, m.p. 184–185°. The spectral data were also in harmony with the supposition that the 2 substances might be identical.

This supposition was verified by direct comparison (mixed melting point and infrared spectra) of pyrethrol with an authentic sample of taraxasterol.[3] The 2 samples were undistinguishable. Pyrethrol is therefore identical with taraxasterol and the former name should be stricken from the literature.

EXPERIMENTAL[4]

Pyrethrol.—Crude pyrethrol crystallized from chloroform–ethanol as colorless needles, m.p. 217–219°, $[\alpha]_D$ +92°, infrared bands at 3400, 1050 (hydroxyl), 1650, 890 cm.$^{-1}$ (exocyclic methylene), NMR signals at 4.65 (broad singlet, $W_{1/2}$ 4 c/s, 2 protons, exocyclic methylene), 3.2 p.p.m. (multiplet, 1 proton, H_3). The infrared spectrum was superimposable on that of an authentic sample of taraxasterol, m.p. 219–221°, mixed m.p. 219–221°.

Derivatives of Pyrethrol.—*Acetate.*—Acetylation of pyrethrol with acetic anhydride and pyridine at 80° for 2 hr. gave a monoacetate which crystallized from chloroform–ethanol as lustrous plates, m.p. 246–248°, $[\alpha]_D$ +105°, infrared bands at 1735, 1250 (acetate), 1650, 890 cm.$^{-1}$ (exocyclic methylene), no hydroxyl absorption, NMR signals at 4.65 (as in pyrethrol above), 4.5 (multiplet, 1 proton, H_3), 2.02 p.p.m. (singlet, 3 protons, acetate).

Benzoate.—Benzoylation of pyrethrol with benzoyl chloride and pyridine at 50° for 2 hr. gave a monobenzoate which crystallized from ethanol as colorless needles, m.p. 244–247°, infrared bands at 1730, 1280 (benzoate), 1650, 890 (exocyclic methylene), 1605, 1595, 715, 690 cm.$^{-1}$ (monosubstituted benzene ring).

Dehydropyrethrol.—A suspension of 0.5 Gm. of pyrethrol in 50 ml. of acetone was treated with Jones reagent at 25° until a brown color persisted. Dilution with water gave a flocculent precipitate which was collected and crystallized from ethanol to furnish 0.41 Gm. of dehydropyrethrol, m.p. 179–182°, infrared bands at 1710 (cyclohexanone), 1650, 890 cm.$^{-1}$ (exocyclic methylene), no hydroxyl absorption, NMR signal at 4.65 (broad singlet, 2 protons, exocyclic methylene).

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[1] For a review of the chemistry of the natural pyrethrins, see *Reference 1*.

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[3] Kindly supplied by Dr. K. Takemoto, Tohoku University, Sendai, Japan, through the courtesy of Dr. M. Matsui, Institute for Physical and Chemical Research, Tokyo, Japan.

[4] Rotations were run in chloroform, infrared spectra in chloroform and as Nujol mulls, NMR spectra in deuterochloroform with tetramethyl silane serving as internal standard.