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SHORT COMMUNICATION

AN EXAMINATION OF THE RUBIACEAE OF HONG KONG—IV.*

THE OCCURRENCE OF TRITERPENOIDS AND TRITERPENOID SAPONINS FROM *ANTIRRHOEA CHINENSIS* (CHAMP.)

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Plant. Antirrhoea chinensis (Champ.) Benth. and Hook.

Uses. Medicinal, for chest complaints.

Previous work. None.

Leaves. (Extrctd light petroleum, chromatographed—alumina):

Friedelin $C_{30}H_{50}O$ (m.p., mxd m.p., $[\alpha]_D$, i.r.): from light petroleum fractions.

Friedelan-3β-ol $C_{30}H_{52}O$ (m.p., mxd m.p., $[\alpha]_D$, and i.r. of alcohol and acetate): from light petroleum: benzene (4:1) fractions.

A higher aliphatic alcohol[1,2,3,*] (m.p., mxd m.p., and i.r. of alcohol and acetate): from light petroleum: benzene (1:1) fractions.

β-Sitosterol $C_{29}H_{50}O$ (m.p., mxd m.p., $[\alpha]_D$, and i.r. of alcohol and acetate): from benzene fractions.

(Extrctd EtOH, evaporated to dryness, extrctd Et_2O, soln. shaken with aq. NaOH, and aq. soln. acidified):

Triterpene acid mixture, methylated and chromatographed (alumina; light petroleum: benzene):

Ursolic acid $C_{30}H_{48}O_3$ (m.p., mxd m.p., $[\alpha]_D$, and i.r. of methyl ester, methyl ester acetate): from light petroleum: benzene (1:4) fractions.

Quinovic acid (Chinovic acid)[4,5] $C_{30}H_{46}O_5$ (m.p., mxd m.p., $[\alpha]_D$, and i.r. of dimethyl ester, dimethyl ester acetate): from early benzene fractions.

Cincholic acid[5] $C_{30}H_{46}O_5$ (m.p., $[\alpha]_D$ of dimethyl ester and dimethyl ester acetate, mxd m.p., i.r. of dimethyl ester acetate) from later benzene fractions.

(Extrctd EtOH, Et_2O insoluble residue):

Saponins, hydrolysed,[6] acid sapogenins methylated to give methyl ester mixture as above, and chromatographed (alumina; light petroleum: benzene): *Ursolic acid, Quinovic acid, Cincholic acid.*

* Part III, *Phytochem.* **6**, (1967).

[1] H. R. ARTHUR, K. F. CHENG, M. P. LAU and K. J. LIE, *Phytochem.* **4**, 969 (1965).
[2] W. H. HUI and C. N. LAM, *Australian J. Chem.* **17**, 493 (1964).
[3] W. H. HUI, C. T. HO and C. W. YEE, *Australian J. Chem.* **18**, 2043 (1965).
[4] *Elsevier's Encyclopaedia of Organic Chemistry*, Vol. 14, p. 526; Vol. 14 *Suppl.*, p. 939*S*. Elsevier, Amsterdam (1940, 1952).
[5] R. TSCHESCHE, I. DUPHORN and G. SNATZKE, *Liebigs Ann. Chem.* **667**, 151 (1963).
[6] M. E. WALL, M. M. KRIDER, E. S. ROTHMAN and C. R. EDDY, *J. Biol. Chem.* **198**, 533 (1952).

New Cpd. Triterpene Acid $C_{30}H_{48}O_4$ (0·0005% of leaves) isolated as methyl ester, m.p. 270–271°, $[\alpha]_D$ +127·1°, ν_{max} 3650, 1740, 1670, 1200, 1146 cm^{-1} (Found: C, 76·66; H, 10·29. $C_{31}H_{50}O_4$ requires: C, 76·50; H, 10·36%): from late fractions on chromatography (ethyl acetate) and crystallization (aq. EtOH).

Sugars: Glucose; Galactose; Glucuronic acid; Galacturonic acid (paper-chromatography of solution after removal of acid sapogenins[7,8,9]).

Stems. (Extrctd light petroleum, chromatographed—alumina):

A higher aliphatic ketone[1,*] (m.p., mxd m.p., i.r.). *Friedelin; Friedelan-3β-ol; A higher aliphatic alcohol;*[1,2,3,*] *β-Sitosterol.*

(Extrctd EtOH)

Ursolic acid; Quinovic acid; Cincholic acid; from Et_2O soluble fraction as for leaves.

Quinovic acid; Cincholic acid; and *Triterpene acid* $C_{30}H_{48}O_4$ (trace) from hydrolysis of Et_2O insoluble saponins as for leaves.

Sugars: Glucose; Galactose; Glucuronic acid; Galacturonic acid, as for leaves.

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[7] F. SANDBERG, B. AHLENIUS and R. THORSEN, *Svensk Farm. Tidskr.* **62**, 541 (1958).
[8] P. COLOMBO, D. CORBETTA, A. PIROTTA, G. RUFFINI and A. SARTORI, *J. Chromatog.* **3**, 343 (1960).
[9] M. T. KRAUSS, H. JÄGER, O. SCHINDLER and T. REICHSTEIN, *J. Chromatog.* **3**, 63 (1960).