

further separated and purified by paper chromatography. All chromatograms were developed by downward migration of the solvent. Whatman No. 3 paper sheets were used for preparative work; for all other purposes Whatman No. 1 chromatography paper was employed.

**Solvent systems.** BFW (*n*-BuOH-HCO<sub>2</sub>H-H<sub>2</sub>O, 20:5:12, upper phase). BAW (*n*-BuOH-HOAc-H<sub>2</sub>O, 4:1:5; upper phase). BEW (*n*-BuOH-EtOH-H<sub>2</sub>O, 4:1:2:2). BBPW (*n*-BuOH-C<sub>6</sub>H<sub>6</sub>-pyridine-H<sub>2</sub>O, 5:1:3:3) 15% HOAc, HOAc-HCl (HOAc-conc HCl-H<sub>2</sub>O, 15:3:82), 1% HCl, Formic (HCO<sub>2</sub>H-conc HCl-H<sub>2</sub>O, 5:2:3), For-estal (HOAc conc HCl-H<sub>2</sub>O, 30:3:10), Phenol (PhOH-H<sub>2</sub>O, 4:1), MAW (MeOH-HOAc-H<sub>2</sub>O, 18:1:1).

**Isolation of pigment.** The pigment used in this study was obtained by collecting the fastest moving band in 15% HOAc of *V. trilobum* L. The use of 1% HCl or other HCl containing solvents were avoided to minimize the occurrence of arabinose as an artifact. The collected pigment band contained Cy-3-xylosylrutinoside as the major anthocyanin and was rechromatographed in BFW for 5 days after elution with MAW. The pigment band appearing on top of the major Cy-3-xylosylrutinoside was collected, pooled, re-run in BFW and finally in 15% HOAc.

**Identification of pigments.** The identification of pigment followed in general the chromatographic and spectroscopic procedure described by Harborne.<sup>4</sup> All pigments and hydrolyzed products were compared with authentic markers on the same chromatograms in several solvent systems. For *R<sub>f</sub>* determinations, the MAW eluate of each pigment was evaporated to dryness, redissolved in 0.5% HCl/MeOH and spotted along with authentic anthocyanins (Cy-3-glucoside from raspberry, Cy-3-sambubioside from red currants, Cy-3-arabinosylglucoside from *V. trilobum* L.<sup>2</sup> and Cy from reductive acetylation<sup>5</sup> of commercial quercetin). Reference trioxide, xylosylrutinoside, was obtained from Cy-3-xylosylrutinoside of red currants by hydrogen peroxide hydrolysis.

<sup>4</sup> HARBORNE, J. B. (1967) *Comparative Biochemistry of the Flavonoids*. Academic Press, New York.

<sup>5</sup> KING, H. G. C. and WHITE, T. (1957) *J. Chem. Soc.* 3701.

---

Phytochemistry, 1974, Vol. 13, pp. 1999 to 2000. Pergamon Press. Printed in England.

## TRITERPENE ACIDS OF INDIAN CLOVE BUDS

C. R. NARAYANAN\* and A. A. NATU

National Chemical Laboratory, Poona-8, India†

(Received 29 December 1973)

**Key Word Index**—*Syzygium aromaticum* (L) Merr.; Caryophyllaceae; triterpene; maslinic acid; naphthalene.

**Previous work.** Isolation of products from the oil of cloves of unspecified origin; the yield of the products are not given.<sup>1-9</sup>

**Present work.** Clove buds (dry, Indian origin) (*Syzygium aromaticum* (L.) Merr., *Eugenia caryophyllata* Thumb.) on steam distillation gave, from the phenolic fraction, eugenol,<sup>1,4</sup> (ca 16%) and from the neutral fraction, caryophyllene<sup>2</sup> (ca 1.6%) and naphthalene (ca 0.1%). As there is only one reference in the literature regarding the isolation of naphthalene

\* Present address: Institut de Chimie, Université Louis Pasteur, Strasbourg, France.

† Communication No.: 1732, National Chemical Laboratory, Poona-8, India.

<sup>1</sup> BONASTRE (1826) *Ann. Chim.* **35**, 274.

<sup>2</sup> SCHREINER, O. and KREMERS, E. (1899) *Pharm. Arch.* **2**, 273, 293.

<sup>3</sup> SODEN, H. V. and ROJAHN, W. (1902) *Pharm. Ztg.* **47**, 779.

<sup>4</sup> REICH, R. (1909) *Z. Nahr. Genussm.*, **18**, 401.

<sup>5</sup> HAAR, A. W. VAN DER (1927) *Rec. Trav. Chim.* **46**, 775, 793.

<sup>6</sup> WINTERSTEIN, A. and STEIN, G. (1932) *Z. Physiol. Chem.* **202**, 222.

<sup>7</sup> TSCHESCHE, R. and POPPEL, G. (1959) *Chem. Ber.* **92**, 320.

<sup>8</sup> CAGLIOTI, L., CAINELLI, G. and MINUTILLI, F. (1961) *Gazz. Chim. Ital.* **91**, 1387.

<sup>9</sup> CAGLIOTI, L. and CAINELLI, G. (1962) *Tetrahedron*, **18**, 1061.

from clove oil,<sup>3</sup> its presence was verified by isolating 0.1% of naphthalene from each of 3 different samples. The content of the steam distillation flask was filtered (the filtrate gave glucose and xylose with smaller amounts of arabinose) and the residue treated with 10% alcoholic NaOH and re-filtered. The filtrate was acidified and the residue obtained was worked up to give oleanolic acid<sup>5,6</sup> (ca 1%), sitosterol (ca 0.1%) and maslinic acid (2 $\alpha$ -hydroxyoleanolic acid) (ca 0.15%); m.p. 262°, [ $\alpha$ ]<sub>D</sub> + 50°, methyl ester, m.p. 227° [ $\alpha$ ]<sub>D</sub> + 60°, methyl ester diacetate m.p. 170°, [ $\alpha$ ]<sub>D</sub> + 34°. The constants are in agreement with literature values.<sup>7-9</sup> The NMR spectra of the last two derivatives show that the two hydroxyl substituents at C<sub>2</sub> and C<sub>3</sub> are equatorial in a chair ring: methyl ester 3 $\alpha$ -H ( $\delta$  3.0, *d*, *J* 10 Hz), C<sub>2</sub> $\beta$ -H ( $\delta$  2.63, b.m.), methyl ester diacetate, C<sub>3</sub> $\alpha$ -H ( $\delta$  4.72, *d*, *J* 10 Hz) and C<sub>2</sub> $\beta$ -H ( $\delta$  4.45, b.m.).

The residue left after the extraction with alcoholic NaOH was analysed and showed Al, Fe, CO<sub>3</sub><sup>''</sup> and oxalate as major and Mg, Si, Cl<sup>'</sup> and SO<sub>4</sub><sup>''</sup> as minor ions.

---

Phytochemistry, 1974, Vol. 13, pp. 2000 to 2001. Pergamon Press. Printed in England.

## TERPENOIDS AND HYDROCARBONS OF *ACROPTILON PICRIS*

YAGHOUB AYNEHCHI and SORAYA ESHAGHZADEH

Department of Pharmacognosy, School of Pharmacy, University of Tehran, Iran

(Received 18 January 1974)

**Key Word Index**—*Acroptilon picris*; Compositae; triterpenes; behenicacid octacosyl ester;  $\alpha$ -euphorpol.

**Plant.** *Acroptilon picris* Pall. (Voucher specimen No. APC 97, Department of Pharmacognosy, School of Pharmacy, University of Tehran, Iran). **Source.** Central part of Iran plateau. **Previous work.** None.

**Results.** Roots, stems, leaves and flowers were air dried, milled, and exhaustively extracted with petrol. (40–60°). The residue was dissolved in petrol. and chromatographed on neutral aluminum oxide (E. Merck). *n*-Nonacosane C<sub>29</sub>H<sub>60</sub> m.p. 62–64° (Found, C, 84.88, H, 14.60. Req'd. C, 85.20, H, 14.80%, m.m.p., TIC, IR and NMR) was found in the earlier petrol fraction and crystallized from MeOH–petrol. The petrol–C<sub>6</sub>H<sub>6</sub> fractions (80–20) gave behenic acid octacosyl ester (from MeOH) C<sub>50</sub>H<sub>100</sub>O<sub>2</sub><sup>1</sup> m.p. 78–80° [(Found, C, 82.06, H, 13.60. Req'd. C, 81.96, H, 13.66%, IR 1730 and 1140 cm<sup>-1</sup>, NMR(CDCl<sub>3</sub>)  $\delta$  4.05 ppm (*t*, *J* 6 Hz, 2H, –CH<sub>2</sub>–O–), 2.26 ppm (*t*, *J* 6 Hz, 2H, –CH<sub>2</sub>–CO–), 1.25 ppm (*s*, 90 H), 0.90 ppm (*s*, 3H, –Me), and 0.65 ppm (*s*, 3H, –Me)]. Hydrolysis gave, octacosanol (m.p., m.m.p., TIC, IR and NMR), and behenic acid (m.p., m.m.p., TIC, IR and NMR). Octacosanol, C<sub>28</sub>H<sub>58</sub>O<sup>2</sup> m.p. 81–83° (Found, C, 81.55, H, 14.12. Req'd. C, 81.67, H, 14.23%, IR, 3418 cm<sup>-1</sup>, m.m.p., TIC, NMR. Acetate and benzoate m.p., m.m.p., IR 1740 cm<sup>-1</sup>) was found in the benzene–CHCl<sub>3</sub> fractions (95–95) and was crystallized from MeOH–acetone

<sup>1</sup> ANEHCHI, Y. and MAHMOODIAN, M. (1973) *Acta Pharm. Suecuca* **10**, 515.

<sup>2</sup> AYNEHCHI, Y., MOJTABAI, M. and YAZDIZADEH, K. (1972) *J. Pharm. Sci.* **61**, 292.