species of this genus were purchased, and the entire freeze-dried plants were screened for alkaloids with TLC using previously reported procedures.[1] In two cases (*G. aguirreanus* and *G. horripilus*) alkaloids were crystallized as hydrochlorides directly from the screening extracts, and in two other cases (*G. roseanus* and *G. roseanus* var.?) alkaloids were crystallized from larger extractions.[2] Alkaloids not crystallized were identified by TLC (cochromatography with reference compounds in five solvent systems on SGG). Hordenine and *N*-methyltyramine have been observed previously in several plant families, but never has such a large concentration of hordenine been reported from members of the Cactaceae.[3] *N*-Methyl-*β*-phenethylamine has been previously reported in the Chenopodiaceae[4] and the Leguminosae,[4,5] and has recently been isolated from members of the cactus genus *Dolichothele*.[1,2] No alkaloids were detected in the *Thelocactus* species. The results are summarized in Table 1.

Acknowledgements—The authors thank Dr. E. F. Anderson for providing plants that initiated the project and Mr. Charles Glass for confirmation of identifications. This work was supported by grants from the National Institutes of Health (GRS Grant No. RRO-5586), the Purdue University Cancer Committee (Indiana Elks), and the Cactus and Succulent Society of America. L.G.W. acknowledges support as a Purdue Scholastic Fellow, 1972–1973.

[1] DINGERDISSEN, J. J. and MCLAUGHLIN, J. L. (1973) *Lloydia* **36**, in press.
[2] DINGERDISSEN, J. J. and MCLAUGHLIN, J. L. (1973) *J. Pharm. Sci.* **62**, 1663.
[3] SATO, P. T., NEAL, J. M., BRADY, L. R. and MCLAUGHLIN, J. L. (1973) *J. Pharm. Sci.* **62**, 411.
[4] WILLAMAN, J. J. and SCHUBERT, B. G. (1961) Alkaloid Bearing Plants and Their Contained Alkaloids, U.S. Dept. Agr., Tech. Bull. No. 1234, U.S. Gov. Print. Office, Washington, D.C.
[5] WILLAMAN, J. J. and LI, H-L. (1970) *Lloydia* **33**, Supplement.

Phytochemistry, 1974, Vol. 13, pp. 666 to 668. Pergamon Press. Printed in England.

HEDERAGENIC ACID AND OTHER CONSTITUENTS OF *VIBURNUM ERUBESCENS**

SANTOSH K. AGARWAL and RAM P. RASTOGI

Central Drug Research Institute, Lucknow, India

(*Received* 24 *September* 1973. *Accepted* 16 *October* 1973)

Key Word Index—*Viburnum erubescens*; Caprifoliaceae; Hederagenic acid; *n*-tritriacontane; *β*-amyrin; sitosterol; oleanonic acid; oleanolic acid; 2*α*-hydroxyursolic acid.

The alcoholic extract of *Viburnum erubescens* Wall. has been reported to show antiviral activity.[1] The chloroform-soluble fraction of the alcoholic extract was defatted with light petroleum and the lipid fraction was subjected to repeated chromatographic separations to obtain substances *A*, *E* and *F*. The defatted chloroform-soluble material was found to contain five compounds *G*, *H*, *I*, *J* and *K* (TLC) which were isolated by column chromatography and preparative TLC.

* CDRI communication No. 1891.

[1] DHAR, M. L., DHAR, M. M., DHAWAN, B. N., MEHROTRA, B. N. and RAY, C. (1968) *Indian J. Expt. Biol.* **6**, 232.

Hederagenic acid (Substance **1**), m.p. 222–225°, $[\alpha]_D$ +75·4°, $C_{30}H_{46}O_4$. IR showed hydroxyl group (3410 cm^{-1}), a carbonyl in 6-membered ring (1715 cm^{-1}), a carboxyl group (1700 cm^{-1}) and a trisubstituted double bond (830 cm^{-1}). It formed methyl ester m.p. 217–218°, $C_{31}H_{48}O_4$ (M^+) *m/e* 484. The NMR of this ester exhibited six quaternary methyls, a primary hydroxyl, and one olefinic proton of the trisubstituted double bond. Its MS showed a strong ion at *m/e* 262 resulting from the retro-Diels Alder fragmentation and base peak at *m/e* 203 as in the case of Δ^{12}-triterpenoids.[2] The fragmentation pattern clearly established that both the primary hydroxyl and carbonyl groups are located in rings A and B of the molecule. The ester formed a monoacetate whose NMR showed the methylene protons of the primary acetoxy groups as a singlet at 4·14 ppm. Sodium borohydride reduction product of the methyl ester showed a multiplet at 2·71 ppm for the methine proton of secondary hydroxyl group in NMR spectrum in addition to other peaks. This diol readily formed a monoacetonide, m.p. 249–251°, $C_{34}H_{54}O_4$, (M^+) *m/e* 526 and was identified as methyl hederagenate (IR, NMR, m.m.p.).

On the basis of above data the new acid (**1**) was established as 3-oxo 23-hydroxyolean-12-en-28-oic acid. This was finally confirmed by comparison with a synthetic sample (hederagonic acid, m.p. 224–225°; methyl ester m.p. 217°) which was obtained by the oxidation of hederagenin with potassium permanganate. It may be mentioned that the literature reports on the identity of hederagonic acid and its methyl ester are ambiguous. This acid, obtained by chromic acid oxidation of hederagenin, has not been characterized and the melting points of the methyl ester are reported[3] as 182° and 217°. This is the second example of a naturally occurring triterpenoid having a keto group at C_3 and a primary hydroxyl function at C_{23}. The first example being icterogenin[4] which was obtained from *Lippia rehmanni*

Substance *A* was obtained as colourless flakes, m.p. 69–70°, and identified as *n*-tritriacontane (GLC, MS). Substance *E*, m.p. 196–198°, R_f 0·53 (C_6H_6). Acetyl derivative, m.p. 240–241°. It was identified as *β*-amyrin (m.m.p., IR and NMR spectra). Substance *F*, m.p. 136°, $[\alpha]_D$ −39° (*c* 2, $CHCl_3$). Acetyl derivative, m.p. 128°. It was confirmed as sitosterol (m.m.p.). Substance *G*, m.p. 160° to 231° depending upon the solvent of crystallization. ν_{max} (KBr): 2900, 2800, 1720, 1710, 1460, 1380, 1360, 1010 and 820 cm^{-1}. NMR: ppm 0·80, 0·90, 0·91, 1·01, 1·13 (3H each, *s*, 5 × Me), 1·00 (6H, *s*, 2 × Me) and 5·33 (1H, *m*, –C=CH). MS: *m/e* 454 (M^+), 439, 203 (base), 189, 187, 133. Methyl ester, m.p. 185–187°. $NaBH_4$ reduction product, m.p. 307–309°. It was confirmed as oleanonic acid (TLC, IR, NMR). Substance *H*, m.p. 309–310°. Methyl ester, m.p. 198–200°. Methyl ester acetate, m.p. 218–220°. It was identified as oleanolic acid (m.m.p., TLC, IR, NMR). Substance *K*, m.p. 242–245°, R_f 0·68 (EtOAc–MeOH, 19:1). Diacetate, m.p. 196–198°. Methyl ester, m.p. 211–213°; Acetonide of methyl ester, m.p. 215–218°. Identified as 2*α*-hydroxy ursolic acid (TLC, IR, NMR and MS).

EXPERIMENTAL

M.ps are uncorrected. R_fs pertain to TLC on Kieselgel G plates.

The alcoholic extract of powdered whole plant (4 kg) (voucher specimen is kept in the Institute) was extracted with $CHCl_3$. The $CHCl_3$-soluble fraction (75·0 g) was exhaustively extracted with petrol to yield an oily fraction *A* (40·0 g) and an insoluble residue *B* (35·0 g).

[2] BUDZIKIEWICZ, H., WILSON, J. M. and DJERASSI, C. (1963) *J. Am. Chem. Soc.* **85**, 3689.

[3] SIMONSON, J. L. and ROSS, W. C. J. (1957) *The Terpenes* Vol. V, pp. 177–178, Cambridge University Press, Cambridge.

[4] BARTON, D. H. R. and DE MAYO, P. (1954) *J. Chem. Soc.* 887.

The fraction *A* (8·0 g) was chromatographed on neutral alumina (activity 2·5, 130 g). The hexane eluate was concentrated and the residue (1·05 g) was repeatedly crystallized from C_6H_6-MeOH as colourless flakes (substance *A*), 68 mg, m.p. 69–70°.

The residue *B* (35 g) was chromatographed over silica gel (700 g) when a C_6H_6–MeOH (3%) fraction was eluate gave colourless needles from alcohol (substance *E*), m.p. 196–198°, 200 mg. The residue from $CHCl_3$ eluates afforded colourless needles from alcohol (substance *F*), m.p. 136°, 40 mg.

The residue *B* (35 g) was chromatographed over silica gel (700 g) when a C_6H_6–MeOH (3%) fraction was obtained which was chromatographed over neutral alumina. The residue (2·09 g) from $CHCl_3$ eluate gave colourless needles from MeOH (substance *G*), m.p. 160–162°, 0·34 g. The residue (2·8 g) from $CHCl_3$–EtOAc (1:1) eluate, containing substances *H*, *I* (*G*, *J*), was rechromatographed on silica gel (75 g) whereby C_6H_6–EtOAc–MeOH (25:10:0·5) eluate crystallized from alcohol (substance *H*), m.p. 309–310°, 80 mg. The subsequent eluates, containing substance *H* and *I*, was applied on preparative silica gel G plates which were developed with C_6H_6–EtOAc–MeOH (25:10:0·5). The residue (70 mg) from the zone containing only substance **1** crystallized from MeOH as colourless needles, m.p. 222–225°.

The C_6H_6–MeOH (5%) eluates gave a residue (2·03 g) which was again chromatographed over silica gel (150 g) and C_6H_6–EtOAc–MeOH (25:10:0·5) eluate yielded colourless needles from alcohol (substance *K*), m.p. 242–245°, 510 mg.

Hederagenic acid. m.p. 222–225°, $[\alpha]_D$ + 75·4° (*c* 0·8, $CHCl_3$). ν_{max} (KBr): 3410, 2900, 2820, 1715, 1700, 1460, 1380, 1356, 1015 and 830 cm^{-1}. (Found: C, 76·40; H, 9·72. $C_{30}H_{46}O_4$ requires: C, 76·59; H, 9·78%). Methyl ester: 217–218°, R_f 0·56 ($CHCl_3$), $[\alpha]_D$ +92° (*c* 1, $CHCl_3$). ν_{max} (KBr): 3400, 2910, 2850, 1735, 1705, 1420, 1390, 810 and 758 cm^{-1}. NMR: ppm 0·84, 0·95 (3H each, *s*, 2 × Me), 1·04, 1·17 (6H each, *s*, 4 × Me), 3·64 (2H, *AB q*, *J* 12 Hz, $-C\underline{H}_2OH$), 3·71 (3H, *s*, –COOMe), 5·42 (1H, *m*, –C=C*H*). MS: *m/e* 484 (M^+), 454, 394, 262, 249, 203 (base), 189, 133, 119 and 105 (Found: C, 76·62; H, 10·01. $C_{31}H_{48}O_4$ requires: C, 76·85; H, 9·91%). Methyl ester acetate: colourless amorphous powder, R_f 0·6 (C_6H_6–$CHCl_3$, 2:1). NMR: ppm 0·83, 0·93, 1·05, 1·16 (3H each, *s*, 4 × Me), 1·01 (6H, *s*, 2 × Me), 2·03 (3H, *s*, OCOMe), 4·14 (2H, *s*, $-CH_2OAc$), 5·42 (1H, *m*, C=C*H*). $NaBH_4$ reduction of methyl ester: Methyl viburnate (50 mg) in EtOH (10 ml) and $NaBH_4$ (50 mg) were stirred together overnight. The reaction mixture (50 mg) showed two spots R_f 0·66 and 0·27 (C_6H_6–EtOAc, 3:1) which were separated by preparative TLC. The major product, R_f 0·66, colourless crystals from C_6H_6–petrol., m.p. 238–240°, 20 mg ν_{max}(KBr): 3600, 2900, 2850, 1735, 1460, 1390, 1048, 804 and 770 cm^{-1}. NMR: ppm 0·82, 1·0, 1·05, 1·18 (3H each, *s*, 4 × Me), 0·95 (6H, *s*, 2 × Me), 2·71 (1H, –C*H*OH), 3·7 (2H, $-C\underline{H}_2OH$), 3·76 (3H, *s*, –COOMe), 5·45 (1H, *m*, –C=C*H*). The $NaBH_4$ reduction product (35 mg) in dry acetone (10 ml) and anhyd. copper sulphate (0·7 g) were shaken overnight at room temp. The resultant acetonide, R_f 0·75 (C_6H_6–EtOAc, 6:1), was obtained as colourless needles from EtOH, 18 mg, m.p. 249–251°. ν_{max}(KBr): 2900, 2830, 1740, 1460, 1390, 1370, 1120 and 870 cm^{-1}. MS: *m/e* 526 (M^+), 511, 466, 451, 262, 203 (base), 133 and 119 (Found: C, 77·52; H, 10·14. $C_{34}H_{54}O_4$ requires: C, 77·74; H, 10·28%).

Acknowledgements—The authors thank Messers R. K. Mukerji, B. B. P. Srivastava, R. K. Singh for IR, NMR and MS data respectively and Mr. Edward Samson for technical assistance.