Leaves. The dried, powdered material was extracted with light petrol. (b.p. 30–60°). The concentrated extract was saponified and worked up as described by Scheuer *et a.*.[13] An ethereal solution of the unsaponifiable fraction was successively extracted with 5% aq. $NaHCO_3$ and 5% aq. KOH solutions, and then evaporated to dryness. The residue was chromatographed on a column of neutral alumina.

The benzene eluate contained a mixture of sitosterol and α-amyrin, resolved by preparative TLC (benzene–Et_2O, 7:3, silica gel G). Sitosterol, $C_{29}H_{50}O$, m.p. 135–137°, $[\alpha]_D$ −35° (L.B. test, m.m.p., IR, co-TLC); acetate, m.p. 125–127°, $[\alpha]_D$ −39° (m.m.p., IR, co-TLC). α-Amyrin, $C_{30}H_{50}O$, m.p. 185–186° (L.B. test of triterpene, TNM, m.m.p., IR, co-TLC); acetate, m.p. 210–220° (m.m.p., IR, co-TLC); α-amyrenone, m.p. 121–123° (2,4-DNPH and TNW tests, IR, co-TLC). More sitosterol was eluted with Et_2O. The benzene–Et_2O (9:1) eluate gave a mixture of three substances resolved by preparative TLC (benzene–MeOH, 4:1, silica gel G) into sitosterol (identified as above), unknown A, m.p. 170–172° (L.B. test of triterpene, TNM, IR acetate, m.p. 62–64°) and of unknown B (trace).

Dilution of the 5% aq. KOH solution followed by cooling furnished taraxasterol, m.p. 222–224° (L.B. test of triterpene, TNM, IR, co-TLC): acetate, m.p. 238–241°; deacetylation product, m.p. 221–223°; benzoate, m.p. 238–241°. Acidification of the alkaline solution, extraction with ether and evaporation of the ethereal extract to dryness yielded unknown C, m.p. 239–241° (dec.), MW 452 (M^+) (L.B. test of triterpene, TNM, IR).

Acknowledgements—The author is grateful to Drs. Heber W. Youngken, Jr. and John J. Tashiro, Department of Pharmacognosy, College of Pharmacy, University of Rhode Island, for their help and interest on this work.

[13] P. J. SCHEUER, C. E. SWANHOLM, L. A. MADAMBA and W. R. HUDGINS, *Lloydia* **26,** 133 (1963).

Phytochemistry, 1973, Vol. 12, pp. 476 to 478. Pergamon Press. Printed in England.

A NOVEL WITHANOLIDE FROM *DATURA QUERCIFOLIA*

K. L. DHAR and M. L. RAINA

Regional Research Laboratory (Branch), Sanat Nagar, Srinagar-5, Kashmir, India

(*Received* 9 *October* 1972. *Accepted* 21 *October* 1972)

Key Word Index—*Datura quercifolia*; Solanaceae; withanolide; daturalactone.

During the chemical investigation of *Withania somnifera* a new type of steroidal lactone has been reported.[1] Recently, similar withanolides have been reported from *Jaborosa integrifolia*.[2,3] In this communication we report the presence of a similar type of withanolide, named here as daturalactone from *Datura quercifolia.*

During the screening of *Datura* species for the alkaloid hyoscine, a novel compound close to withanolides in structure was extracted from leaves of *D. quercifolia* HBK with benzene and purified by repeated crystallization from light petrol.–benzene mixture (1:1).

[1] D. LAVIE, I. KIRSON and E. GLOTTER, *Israel J. Chem.* **6,** 671 (1968).
[2] R. TSCHESCHE, K. ANNEN and P. WELZEL, *Chem. Ber.* **104,** 3556 (1971).
[3] R. TSCHESCHE, K. ANNEN and P. WELZEL, *Tetrahedron* **28,** 1909 (1972).

Element analysis and MS analysis of daturalactone m.p. 260–261°, $[\alpha]_D$, 0° (*c*, 0·50; $CHCl_3$) established the molecular formula as $C_{28}H_{38}O_7$. The IR exhibited band at 1695 and 1729 cm^{-1} attributed to α–β-unsaturated carbonyl and to a 6-membered unsaturated lactone carbonyl, respectively, a broad multiple band between 3300 and 3600 cm^{-1}, most of which remains even after acetylating the compound; indicating the presence of both secondary and tertiary hydroxyls. The acetylated product on purification gives a mono-acetate m.p. 248°, (M^+) 528, *m/e* 468 (M − 60), indicating the presence of only one secondary alcohol.

In UV it shows strong absorption at 223 nm. The compound on hydrogenation over Pd–C (5%) rapidly absorbed 1 mol H_2. The hydrogenated product (purified by preparative TLC) $C_{28}H_{40}O_7$, m.p. 235–236° (M^+) 488, showed a weak absorption in UV at 227 nm indicating the presence of α–β-unsaturated lactone even after hydrogenation. The initial strong absorption at 223 nm is due to the overlapping of two chromophores,[1] the α–β-unsaturated ketone in ring A and the unsaturated lactone.

The NMR (100 M Hz) in $CDCl_3$ gave bands at (δ): 5·81 *dq* (10:3:1) due to 2H; 6·60 *dq* (10:4·5:3), 3H; 3·06 *d*(4), 6H; 3·35 *d* (4:1), 7H; 4·0 *m* (in acetate → 5·08), 12H; 4·55 *m*, 22H; and methyl group signals for 18H, 19H, 21H, 27H and 28H at 0·88 *s*, 1·18 *s*, 1·02 *d*(5), 1·50 *s* and 1·58 *s* respectively. Chemical shifts are in δ units; coupling constants (in Hz) are given in brackets).

From the above data the new compound appears to be very close to 5α,17α-dihydroxy-1-oxo-6α,7α-epoxy-22*R*-witha-2,24-dienolide reported by Lavie[4] except for the NMR signals due to 27 and 28 methyl protons, which appear very much upfield in the present compound, and the signal due to 12-H. In all the reported withanolides, the stereochemistry of C-22 has been established by CD measurements as *R*. From the molecular models it is clear that when the stereochemistry at C-22 is *R*, the 27 and 28 methyls take the position away from the rest of the molecule, and lie almost in the same plane, while, if C-22 is put as *S*, the plane of the whole lactone ring lies at about 90° with respect to C-(20)–C-(22) bond, with the result that 27 and 28 methyls[5a] the rest of the molecule and in NMR, therefore, appear in the upfield. This can be diagnostic for establishing the stereochemistry at C-22 positions. However, this requires further confirmation by ORD studies.

Daturalactone ono xidation with Jones reagent gives a compound $C_{28}H_{36}O_7$, (m.p. 303–305°, (M^+) 484, the NMR of which is interesting to note. It shows 18-methyl protons to have moved down-field to δ 1·085 (chemical shift of 0·375 Hz) and 21 methyl proton doublet moves upfield to δ 0·89. The only position for –CO which can effect simultaneously 18 and 21 methyl protons is at C-12. So the only secondary hydroxyl is at C-12 position. The signal at δ 4·00 due to 12-H cannot be resolved. However, from the width of its signal at half length (W_H, 5·7 Hz), it is clear that 12H has an equatorial position because as such 12H bisects the 11-methylene protons almost equally resulting into weak splitting (2·5 Hz).[5b,6]

It is further interesting to note that when the NMR spectrum is taken in C_6D_6, all the methyl protons with an exception of 28 methyl protons; move upfield indicating the vicinity of oxygen function close to all methyls except 28-methyl.

[4] I. KIRSON, E. GLOTTER and D. LAVIE, *J. Chem. Soc.* C, 2032 (1971).
[5] N. S. BHACCA and D. H. WILLIAMS, *Application of NMR Spectroscopy in Organic Chemistry*, (a) p. 16; (b) p. 79, Holden-Day (1964).
[6] L. M. JACKMAN and S. STERNHELL, *Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, p. 288, Pergamon Press, Oxford (1969).

MS showed molecular ion at 486 and other fragments at *m/e* 468 (M − 18), *m/e* 450 (M-2 × 18) *m/e* 432 (M-3 × 18) confirming the presence of 3-hydroxyls. The base peak at *m/e* 152 is due to the cleavage of whole side chain (less one H). Characteristic fragments induced by the 17-OH at *m/e* 209 (II) is highly diagnostic as proposed by Prof. Lavie.[4] From the above data daturalactone can be assigned the structure: 5α,12α,17α,trihydroxy-1-oxo-6α,7α-epoxy-22*S*-witha-2,24-dienolide (I).

EXPERIMENTAL

Extraction and isolation procedure. Crushed and dried leaves of *Datura quercifolia* (1·5 kg) were extracted with benzene. The cold extract was concentrated and allowed to stand at 0° for 24 hr; when a light green crystalline substance (1 g) was obtained. This was purified by passing it through a silica gel column. Elution with benzene–EtOAc (1:1) yielded a compound which was crystallized from light petrol.–benzene (1:1) m.p. 260–261°, showing a single spot on TLC (R_f 0·3, EtOAc–benzene, 1:1) (Calc. for $C_{28}H_{38}O_7$: C, 69·13; H, 7·82. Found: 68·87; H, 7·74%) (M^+) 486.

Daturalactone monoacetate. (Ac_2O and pyridine). Colourless shining crystals m.p. 248°, (M^+) 528 (Calc. for $C_{30}H_{40}O_8$: C, 68·19; H, 7·58. Found: C, 67·98; H, 7·53%).

Hydrogenation. The compound was hydrogenated (1 mol H_2) over (5%) Pd–C in EtOH. The hydrogenated product (purified by preparative TLC) crystallized from EtOAc, m.p. 235–236°, λ_{max} 227 nm. (Calc. for $C_{28}H_{40}O_7$: C, 68·85; H, 8·2. Found: C, 68·62; H, 8·0%) (M^+) 488.

Oxidation. The compound in acetone was oxidized with Jones reagent at 0°. Working up as usual and crystallization from hexane–EtOAc (1:1) yielded colourless shining crystals, m.p. 303–305°. (Calc. for $C_{28}H_{36}O_7$: C, 69·42; H, 7·44. Found: C, 69·21; H, 7·24) (M^+) 484.

Acknowledgements—We thank Dr. Orrell, Dr. M. Davies, Dr. U. Ragnasson for the spectral data, Dr. B. K. Bhat for the plant material, A. M. Chisti for technical assistance and Director of this laboratory for permitting M.L.R. to work in this laboratory.