Phytochemistry, Vol. 24, No. 10, pp. 2456–2457, 1985.
Printed in Great Britain.

0031-9422/85 $3.00 + 0.00
Pergamon Press Ltd.

TORVONIN-A, A SPIROSTANE SAPONIN FROM *SOLANUM TORVUM* LEAVES

UMAR MAHMOOD, PAWAN K. AGRAWAL and RAGHUNATH S. THAKUR

Central Institute of Medicinal and Aromatic Plants, Lucknow-226016, India

(*Revised received* 11 *March* 1985)

Key Word Index—*Solanum torvum*; Solanaceae; steroidal saponin; torvonin-A; neochlorogenin-3-*O*-β-L-rhamnopyranosyl (1 → 2)-β-L-rhamnopyranoside.

Abstract—A new steroidal saponin, torvonin-A, has been isolated from *S. torvum* leaves and its structure has been established as neochlorogenin-3-*O*-β-L-rhamnopyranosyl (1 → 2)-β-L-rhamnopyranoside.

INTRODUCTION

We have recently reported the isolation of several spirostanes [1] and aliphatic hydrocarbon derivatives [2] from the leaves of *S. torvum*. Further investigations led to the isolation of a new steroidal saponin named torvonin-A. The present communication deals with its isolation and characterization.

RESULTS AND DISCUSSION

The chloroform extract of the leaves of *Solanum torvum*, on repeated chromatographic purification, afforded a saponin **1** which gave a positive Liebermann–Burchard test but did not respond to Ehrlich's reagent. On acid hydrolysis of **1**, neochlorogenin (IR, ^{1}H NMR, MS and comparison with an authentic sample) and rhamnose (PC) were obtained. It readily formed a hexaacetyl derivative **2**. The mass spectrum of **2** showed the characteristic fragment at *m/z* 503 for the pentaacetyl rhamnobioside moiety, in addition to ion peaks at *m/z* 273, 189, 171, 153 and 111 assigned to the triacetyl rhamnose moiety [3]. The prominent ion peaks at *m/z* 139 and 115 suggested an intact spirostane skeleton unsubstituted in the E and F rings [3].

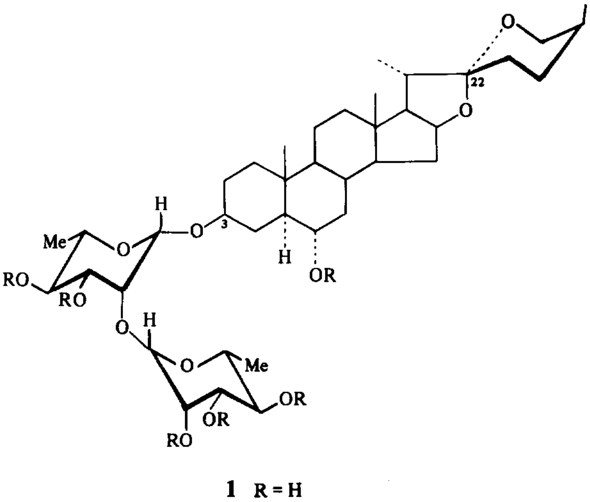
The 400 MHz ^{1}H NMR spectrum of **1** exhibited two singlets at δ0.80 (H-18) and 0.83 (H-19), and two doublets (J = 7 Hz) at 1.04 (H-21) and 1.16 (H-27), as well as two more secondary methyl group signals at 1.60 and 1.69 due to the methyl groups of the rhamnose unit [4]. The anomeric proton signals observed at δ4.75 as a doublet (J = 8 Hz) and at 4.81 ($W_{1/2}$ = 4 Hz) as a broad singlet clearly demonstrated the β-anomeric configuration [5–7].

The proton noise decoupled ^{13}C NMR spectrum of **1** showed 39 carbon signals. The number of attached hydrogens to each individual carbon atom was determined from the DEPT technique which suggested the presence of 20 × CH, 10 × CH_2, 6 × Me and three quaternary carbon atoms, hence inferring the presence of a disaccharide moiety in **1**. The ^{13}C NMR shielding data were analysed by analogy with the literature reports for steroidal sapogenins and saponins [8–13] which further confirms the identity of the genin as neochlorogenin. However, it might be worth mentioning here that the assignments for C-23 and C-25 as reported by Chakravarty *et al.* [12] should be reversed in view of the nature of the carbon signal as established by the DEPT experiment. By comparison with the published data [14], the ^{13}C NMR spectrum of **1** showed it to be a β-L-rhamnopyranoside (Table 1) and the glycosidic linkage between the two rhamnose units was (1 → 2) as the C-2 resonance of the inner rhamnose unit had an 11.21 ppm downfield shift, and the C-3 resonance a 4.79 ppm upfield shift compared to the equivalent values of methyl-*O*-β-L-rhamnopyranoside [14]. Considering all the above evidence, torvonin-A was identified as neochlorogenin-3-*O*-β-L-rhamnopyranosyl (1 → 2)-β-L-rhamnopyranoside (**1**).

EXPERIMENTAL

Mp uncorr; IR: KBr; ^{1}H NMR: 400 MHz (pyridine-d_5) TMS as internal standard; ^{13}C NMR: 100 MHz (pyridine-d_5); TLC: silica gel G, the spots were visualized by Liebermann–Burchard reagent and by spraying with 50% H_2SO_4.

Solanum torvum leaves were collected from Dehradun, U.P.



1 R = H
2 R = Ac

Table 1. ^{13}C NMR chemical shifts (δ in ppm) of torvonin-A

Carbon No.		Carbon No.		Carbon No.	
1	37.76	15	33.16*	3-rha	
2	32.12*	16	81.11	1	103.04
3	79.44	17	40.78	2	83.41
4	32.24*	18	16.62	3	70.63
5	51.31	19	13.58	4	74.16
6	69.91	20	42.49	5	72.72
7	41.43	21	14.86	6	18.64
8	34.18	22	109.64	(1→2)-rha	
9	53.88	23	26.41	1	105.59
10	36.73	24	26.21	2	72.59
11	21.27	25	27.54	3	76.21
12	40.07	26	65.09	4	75.23
13	40.78	27	16.30	5	72.76
14	56.39			6	18.78

*Mutually exchangeable assignments.

(India). A voucher specimen is deposited in CIMAP Herbarium collection No. 249.

Extraction and isolation of saponin. The air dried leaves (5.5 kg) were powdered and extracted at room temp by stirring for 16 hr with *n*-hexane (5 × 7 l.) followed by MeOH (5 × 7 l.). The MeOH extract was concd to 500 ml. Water (1 l.) was added and the mixture extracted with $CHCl_3$ (5 × 1 l.). The $CHCl_3$ extract was concd to dryness (122 g) and part of the extractive (60 g) was chromatographed over silica gel (1.8 kg, BDH, 60–120 mesh) eluting with hexane, hexane–C_6H_6 (1:1), (1:3), C_6H_6, C_6H_6–$CHCl_3$ (3:1, 1:1, 1:3), $CHCl_3$, $CHCl_3$–MeOH (99:1, 98:2, 96:4, 95:5, 90:10, 85:15 and 80:20); the eluate was collected in 500 ml portions.

The fraction obtained as a result of elution with $CHCl_3$–MeOH (85:15) gave a white residue (4.5 g) which exhibited the presence of two spots with very close R_f values on TLC. Further fractionation of this residue on a silica gel column using $CHCl_3$–MeOH–H_2O (60:17:10, organic layer) as eluent resulted in the isolation of torvonin-A (45 mg). Torvonin-A (**1**) colourless powder, mp 285°; $[\alpha]_D = -37.3°$ (*c* 0.30; pyridine); IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3500–3300 (broad, OH), 1380, 1220, 1170, 1150–1000 (C–O–C), 982, 918, 892 and 850 (918 > 892, 25S spiroketal). ^{1}H NMR: δ0.80 (3H, *s*, H-18), 0.83 (3H, *s*, H-19), 1.04 (3H, *d*, J = 7 Hz, H-21), 1.16 (3H, *d*, J = 7 Hz, H-27), 1.60 (3H, *d*, J = 6 Hz, rha-Me), 1.69 (3H, *d*, J = 6 Hz, rha-Me), 3.14 (1H, *d*, J = 12 Hz, H-4α H), 3.32 (1H, *d*, J = 11 Hz, H-26β), 3.56–3.75 (6H, *m*, H-3α, H-6β, 4 × rha-H), 4.00 (2H, *m*, H-26α, rha-H), 4.28 (1H, *t*, J = 9 Hz, rha-H), 4.33 (1H, *t*, J = 9 Hz, rha-H), 4.49 (1H, *q*, J = 8 Hz, H-16α), 4.59 (1H, *dd*, J = 9, 4 Hz, rha-H), 4.75 (1H, *d*, J = 8 Hz, rha-H), 4.81 (1H, *br s*, $W_{1/2}$ = 4 Hz, rha-H). ^{13}C NMR: see Table 1.

Acetylation of compound **1**. Compound **1** was acetylated with Ac_2O–pyridine at room temp and, after the usual work up, gave a hexaacetate **2**. IR $\nu_{\text{KBr}}^{\max}$ cm^{-1}: 2940, 2842, 1735, 1450, 1380, 1235–1210 (broad), 980, 920, 905, 880 and 850. MS m/z (rel. int.): 976 $[M]^+$ (absent), 856 $[M-2AcOH]^+$ (0.2), 503 (16.5), 273 (76.8), 189 (10), 171 (22.2), 153 (16.5), 139 (52.2), 115 (10.3), 111 (45.5), 42 (100).

Acid hydrolysis of compound **1**. Compound **1** was hydrolysed with Kiliani mixture (AcOH–HCl–H_2O, 1.5:3.5:5) as well as 7% methanolic H_2SO_4 and was worked up as usual. The aq. portion revealed the presence of only rhamnose on PC (BuOH–AcOH–H_2O, 4:1:5) by comparison with an authentic sample, while the aglycone was identified as neochlorogenin by comparison with an authentic sample (mp, mmp, Co-TLC, IR, NMR and MS).

Acknowledgements—We are thankful to Dr. A. Hussin, Director, CIMAP, for the necessary facilities and to Prof. H. J. Schneider, Universität, Saarbrücken, F. R. Germany for ^{1}H NMR and ^{13}C NMR data. One of us (U.M.) thanks CSIR, New Delhi, for the award of a research associateship.

REFERENCES

1. Mahmood, U., Thakur, R. S. and Blunden, G. (1983) *J. Nat. Prod.* **46**, 427.
2. Mahmood, U., Shukla, Y. N. and Thakur, R. S. (1983) *Phytochemistry* **22**, 167.
3. Chakravarty, A. K., Saha, C. R. and Pakrashi, S. C. (1979) *Phytochemistry* **18**, 902.
4. Watanabe, Y., Sanada, S., Ida, Y. and Shoji, J. (1983) *Chem. Pharm. Bull.* **31**, 1980.
5. Kasai, R., Okihara, M., Asakawa, J., Mizutani, K. and Tanaka, O. (1979) *Tetrahedron* **35**, 1427.
6. Miyamura, M., Nakano, K., Nohara, T., Tomimatsu, T. and Kawasaki, T. (1982) *Chem. Pharm. Bull.* **30**, 712.
7. Haroda, K., Ito, S. and Suzuki, M. (1982) *Chem. Pharm. Bull.* **30**, 4288.
8. Agrawal, P. K., Singh, S. B. and Thakur, R. S. (1984) *Indian J. Pharm. Sci.* **46**, 158.
9. Eggert, H. and Djerassi, C. (1975) *Tetrahedron Letters* 3635.
10. Tori, K., Seo, S., Terui, Y., Nishikawa, J. and Yasuda, E. (1981) *Tetrahedron Letters* **22**, 2405.
11. Elgamal, M. H. A., Bedour, M. S. and Duddeck, H. (1980) *Indian J. Chem.* **19B**, 549.
12. Chakravarty, A. K., Pakrashi, S. C. and Uzawa, J. (1981) *Can. J. Chem.* **59**, 1328.
13. Agrawal, P. K., Jain, D. C., Gupta, R. K. and Thakur, R. S. (1985) *Phytochemistry* (in press).
14. Seo, S., Tomita, Y., Tori, K. and Yoshimura, Y. (1978) *J. Am. Chem. Soc.* **100**, 3331.