1-(4′-*hydroxy*-2′-*methoxy*-5′-*methylphenyl*)-3-(2″-*hydroxy*-4″,5″-*methylenedioxyphenyl*)-*Propane* (**2d**). ^{13}C NMR [50.3 MHz, $(CD_3)_2CO$)] δ: 28.2 (C-1), 29.5 (C-2), 27.5 (C-3), 119.4* (C-1′), 154.9 (C-2′), 97.5 (C-3′), 152.7 (C-4′), 113.7 (C-5′), 130.2 (C-6′), 119.6* (C-1″), 148.2 (C-2″), 96.2 (C-3″), 144.3 (C-4″), 138.8 (C-5″), 107.9 (C-6″), 13.3 (Me-5′), 53.6 (OMe), 99.2 (O_2CH_2); *signals may be interchanged.

1-(2′,4′-*dihydroxy*-6′-*methoxy*-3′,5′- *dimethylphenyl*)-3-(2″-4″,5″-*methylenedioxyphenyl*)-*Propane* (**2e**). Oil. IR ν_{max}^{film} cm^{-1}: 3418, 1607, 1505, 1483, 1442, 1383, 1226, 1171, 1097, 1039, 991, 934, 855, 761. ^{1}H NMR [200 MHz, $(CD_3)_2CO$] δ: 2.55–2.45 (*m*, H-1,1,3,3), 1.80–1.75 (*m*, H-2,2), 2.09 (*s*, Me-5′), 2.11 (*s*, Me-3′), 3.59 (*s*, OMe), 5.82 (*s*, O_2CH_2), 6.42 (*s*, H-3″), 6.61 (*s*, H-6″), 6.97, 7.03, 7.93 (3*s*, 3OH). ^{13}C NMR [50 MHz, $(CD_3)_2CO$] δ: 30.7 (C-1), 31.5 (C-2), 29.4 (C-3), 114.9 (C-11, correlated at long range with H-1), 152.4 (C-2′, corr. H-1), 108.0 (C-3′, corr. Me-3′), 152.8 (C-4′, corr. Me-3′), 109.5 (C-5′, corr. Me-5′), 156.2 (C-6′, corr. H-1, Me-5′, OMe), 121.6 (C-1″, corr. H-3, H-3″), 150.1 (C-2″, corr. H-3″, H-6″, O_2CH_2), 98.4 (C-3″, corr. H-3″), 146.5 (C-4″, corr. H-3″, H-6″, O_2CH_2), 141.2 (C.5″, corr. H-3″, H-6″, O_2CH_2), 109.9 (C-6″, corr. H-3, H-6″), 9.5 (Me-3′), 9.3 (Me-5′), 60.9 $O\underline{C}H_3$, corr. $OC\underline{H}_3$), 101.3 ($O_2\underline{C}H_2$, corr. $O_2C\underline{H}_2$).

REFERENCES

1. Conserva, L. M., Yoshida, M., Gottlieb, O. R., Martinez V., J. C. and Gottlieb, H. E. (1990) *Phytochemistry* **29**, 3911.
2. Lima, O. A., Gottlieb, O. R. and Magalhães, M. T. (1972) *Phytochemistry* **11**, 2031.
3. Gottlieb, O. R., da Silva, M. L. and Ferreira, Z. S. (1975) *Phytochemistry* **14**, 1825.
4. Vieira, P. C., Yoshida, M., Gottlieb, O. R., Paulino-Filho, H. F., Nagem, T. J. and Braz-Filho, R. (1983) *Phytochemistry* **22**, 711.
5. Diaz, D., P. P. and Diaz A. M. P. de (1986) *Phytochemistry* **25**, 2395.
6. Lima, R. A. de, Franca, N. C., Diaz D., P. P. and Gottlieb, O. R. (1975) *Phytochemistry* **14**, 1831.
7. Moraes, A. A. de, Braz-Filho, R. and Fraiz Jr., S. V. (1989) *Phytochemistry* **28**, 239.

Phytochemistry, Vol. 29, No. 12, pp. 3988–3991, 1990
Printed in Great Britain.

0031–9422/90 $3.00 + 0.00
Pergamon Press plc

TWO FLAVONOL GLYCOSIDES FROM *CHENOPODIUM AMBROSIOIDES*

NEERU JAIN, M. SARWAR ALAM,* M. KAMIL, M. ILYAS, M. NIWA† and A. SAKAE†

Section of Natural Products, Department of Chemistry, Aligarh Muslim University, Aligarh 202 002, India; †Faculty of Pharmacy, Meijo University, Tempaku, Nagoya 468, Japan

(*Received* 15 *March* 1990)

Key Word Index—*Chenopodium ambrosioides*; Chenopodiaceae; kaempferol 3-rhamnoside-4′-xyloside; kaempferol 3-rhamnoside-7-xyloside; isorhamnetin; quercetin.

Abstract—Two new flavonol glycosides, kaempferol 3-rhamnoside-4′-xyloside and kaempferol 3-rhamnoside-7-xyloside along with kaempferol, isorhamnetin and quercetin have been identified from the fruits of *Chenopodium ambrosioides*. Their structures were established using spectroscopic and chemical evidence.

INTRODUCTION

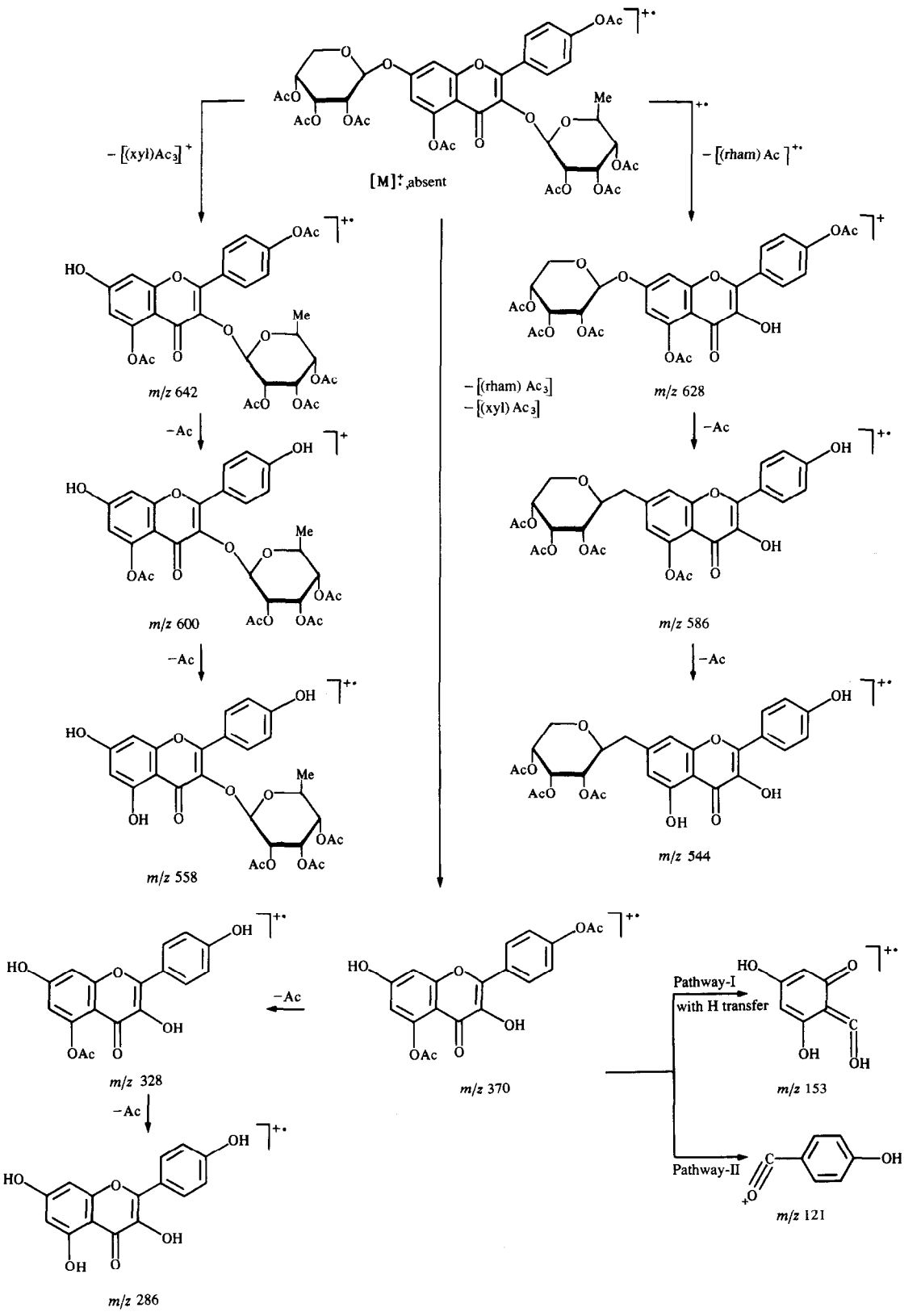
The genus *Chenopodium* consists of *ca* 120 species, 45 of which are distributed in India. *Chenopodium ambrosioides* L. is reported to possess many medicinal properties [1]. The plant is used as an anthelmintic and is particularly effective in expulsion of hookworms. Previous work on the flavonoid chemistry of the genus is scanty [2–6]. We now report two new flavonol glycosides (**1**, **2**) along with kaempferol, isorhamnetin and quercetin from the fruits of *C. ambrosioides*.

*Author to whom correspondence should be addressed.

RESULTS AND DISCUSSION

The ethyl acetate soluble portion of the defatted methanolic extract showed five spots on TLC (silica gel, EtOAc–Me_2CO–HOAc–H_2O, 30:3:1:1). The mixture was resolved into individual components by repeated column chromatography followed by preparative TLC using the same solvent system.

Compound **1** analysed for $C_{26}H_{28}O_{14}$. Its IR spectrum showed strong absorption bands at 3420 (OH), 1655 (C=O), 2950 (C–H), 1620 (C=C, aromatic) and a broad band at 1110–1000 cm^{-1} indicating its glycosidic nature. Colour reactions (dull ochre to fluorescent yellow in UV + NH_3), R_f values and UV spectral data with diagnostic shift reagents [7, 8] suggested it is a 3,4′-disubstituted flavonol glycoside with free hydroxyl groups at the 5 and


[M]+, absent
– [(xyl)Ac3]+
– [(rham) Ac]+•
m/z 642
m/z 628
–Ac
– [(rham) Ac3]
– [(xyl) Ac3]
m/z 600
m/z 586
m/z 558
m/z 544
m/z 328
m/z 370
m/z 286
Pathway-I
with H transfer
m/z 153
Pathway-II
m/z 121

7-positions. Total acid hydrolysis of **1** with 2 M HCl yielded an equimolar mixture of L-rhamnose, D-xylose (PC and GLC) and kaempferol (spectral and chromatographic comparison, [9]).

The glycoside (**1**) formed a crystalline octaacetate, mp 125–127°. The ^{1}H NMR spectrum of the acetate showed the expected signals in the aromatic region. Two *meta* coupled doublets at δ6.79 and δ7.09 (J = 2.2 Hz) were attributed to C-6 and C-8 protons, respectively. Two *ortho* coupled doublets at δ7.90 (J = 8.5 Hz) and δ7.28 (J = 8.5 Hz) which corresponded to the AA'BB' pattern were assigned to C-2',6' and C-3',5' protons of the B-ring. The anomeric protons at δ5.19 (J = 9.5 Hz) and δ5.63 (J = 1.2 Hz) were assigned to H-1 xylose (β-configuration) and H-1 rhamnose (α-configuration), respectively. The rhamnosyl methyl appeared as a doublet at δ1.23 (J = 6.1 Hz). The remaining sugar protons were observed in the range δ3.77–5.60.

The mass spectrum of the acetylated glycoside was in agreement with the assigned structure. The mass spectrum showed the presence of a acetylated pentopyranoside, m/z 259 and acetylated hexopyranoside, m/z 273. The fragment ions observed at m/z 642 and m/z 628 accounted for the loss of acetylated pentopyranoside and hexopyranoside, respectively, from the molecular ion. The loss of both acetylated sugar moieties gave a fragment at m/z 370. The aglycone fragment was observed at m/z 286. A retro-Diels–Alder fragmentation pattern was observed at m/z 153 and m/z 121 leading to fragments $[A_1 + H]$ and B_2^+. The result supported the presence of two hydroxyl groups in ring-A and one hydroxyl group in ring-B.

Enzymatic hydrolysis of **1** with β-xylosidase gave D-xylose and a partial glycoside (**3**) which was identified as kaempferol 3-rhamnoside by UV diagnostic shift reagents and co-chromatography with an authentic sample. On the basis of these data, **1** was identified as kaempferol 3-α-rhamnopyranoside-4'-β-xylopyranoside, which is a new natural product.

Compound **2**, analysed for $C_{26}H_{28}O_{14}$ and gave all colour reactions given by **1**. The striking similarity of IR, ^{1}H NMR and EI mass spectrum between **1** and **2** suggested that they have same chromophore. The UV spectrum and its changes in the presence of diagnostic shift reagents [7, 8] pointed to the presence of a free hydroxyl group at C-5 and C-4' on a 3,7-disubstituted flavonol glycoside framework.

Total acid hydrolysis of the glycoside (**2**) with 2 M HCl gave an equimolar mixture of L-rhamnose, D-xylose and kaempferol. Enzymatic hydrolysis of **2** with β-xylosidase gave the same products as **1**. However, a bathochromic shift of 12 nm in band II with NaOAc (absent in glycoside) indicated that D-xylose was attached at the C-7 position in **2**. Methylation and subsequent acid hydrolysis gave similar products as identified for **1**. On the basis of these findings, **2** was identified as kaempferol 3-α-rhamnopyranoside 7-β-xylopyranoside, which is a new natural product.

The remaining constituents, kaempferol, isorhamnetin and quercetin were identified by standard procedures and direct comparison with authentic samples.

EXPERIMENTAL

General. Mps: uncorr. UV spectra were run in MeOH and IR spectra in KBr discs. ^{1}H NMR spectra were run at 400 MHz. Chemical shifts are given in δ (ppm) with TMS as int. standard. MS were obtained by electron impact at 70 eV. TLC was performed using silica gel G (BDH). Whatman No. 1 paper was used in PC. The TLC spots were visualized in UV light, $FeCl_3$ spray or by exposure to I_2 vapours.

Plant material. The fruits of *Chenopodium ambroisiodes* L. were collected from Aligarh Muslim University campus and authenticated by Prof. Wazahat Hussain.

Extraction and isolation. Fresh fruits (3 kg) were defatted by extraction with hot petrol (40–60°) and the residues were extracted with hot MeOH. The combined concd methanolic extract was dissolved in boiling H_2O, cooled and successively extracted with Et_2O, EtOAc and *n*-BuOH. The EtOAc fraction on TLC (silica gel, EtOAc–Me_2CO–HOAc–H_2O, 30:3:1:1) showed five spots. The mixture was resolved into individual components by repeated CC followed by PTLC using the same solvent system.

Kaempferol 3-α-rhamnopyranoside-4'-β-xylopyranoside (**1**). Pale yellow powder, mp 262–263°. Found C 56.15, H 5.08. $C_{26}H_{28}O_{14}$ requires C 56.11, H 5.03%. UV λ_{max}^{MeOH} nm: 242sh, 269, 315sh, 345; +$AlCl_3$ 250sh, 275, 305sh, 340, 398; +$AlCl_3$–HCl 277, 299, 340, 395; +NaOMe 255sh, 296, 355, 405; + NaOAc 280, 354, 395; + NaOAc–H_3BO_3 271, 318sh, 352. IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1655 (C=O), 2950 (C–H), 1620 (C=C), 1110–1000 (C–O).

Acetylation of **1**. Compound **1** was acetylated with Ac_2O–pyridine (1:1) at room temp. for 48 hr and worked-up in the usual way. The product was purified by prep. TLC on silica gel (C_6H_6–Me_2CO, 7:3) to give an amorphous powder, which was cryst. from petrol–$CHCl_3$ as cream needles, mp 125–127° ^{1}H NMR ($CDCl_3$) δ:6.79 (1H, *d*, J = 2.2 Hz, H-6); 7.09 (1H, *d*, J = 2.2 Hz, H-8), 7.90 (2H, *d*, J = 8.5 Hz, H-2',6'), 7.28 (2H, *d*, J = 8.5 Hz, H-3',5'), 5.19 (1H, *d*, J = 9.5 Hz, H-1 xylose), 5.63 (1H, *d*, J = 1.2 Hz, H-1 Rham), 1.23 (3H, *d*, J = 6.1 Hz, Rham-Me), 3.77–5.63 (10H, *m*, Gly-H), 2.45 (3H, *s*, OAc-5), 2.34 (3H, *s*, OAc-7), 1.98–2.20 (18H, *m*, aliphatic MeCO). MS EIMS (70 eV) m/z 642 [M − acetylated pentose + H^+]$^+$, 628 [M − acetylated hexose + H]$^+$, 370 [M − acetylated pentose − acetylated hexose + 2H]$^+$, 628 [M − acetylated hexose + H]$^+$, 370 [M − acetylated pentose − acetylated hexose + 2H]$^+$, 286 [M − 614]$^+$, 273 [(Rham)Ac_3]$^+$, 259 [(Xyl)Ac_3]$^+$, 153 $[A_1 + H]^+$, 121 $[B_2]^+$.

Enzymatic hydrolysis of **1**. A mixture of **1** (100 mg) and β-xylosidase (10 mg) was incubated in $(NH_4)_2SO_4$–NaOAc buffer (pH 5.0) at 25° for 30 hr and after addition of H_2O was extracted with *n*-BuOH. The BuOH extract was chromatographed on a silica gel column to give a partial glycoside (**3**) mp 170–172°, identified as kaempferol 3-rhamnoside. From the H_2O layer, D-xylose was identified by PC (four solvents).

Methylation of **3** *followed by acid hydrolysis.* MeI (1 ml) and Ag_2O (30 mg) were added to a solution of **3** (30 mg) in DMF (3 ml). The mixture was stirred in dark at room temp. for 48 hr, filtered and the residue washed with DMF. The filtrate was evapd to dryness, the residue dissolved in ethanol (25 ml). The alcohol was recovered and the syrupy residue hydrolysed with 2 M HCl. On usual work-up it gave kaempferol 5,7,4'-trimethyl ether (14 mg), mp 135–136°. Calc. for $C_{18}H_{16}O_6$: C 65.85, H 4.87. Found; C 65.96, H 4.98%.

Kaempferol 3-α-rhamnopyranoside-7-β-xylopyranoside (**2**). Pale yellow powder, mp 300°. Found C 56.30, H 5.09. $C_{26}H_{28}O_{14}$ requires C 56.11, H 5.03%. UV λ_{max}^{MeOH} nm: 238sh, 260, 310sh, 360; +$AlCl_3$ 244sh, 274, 306, 359sh, 408; +$AlCl_3$–HCl 265, 290sh, 356, 403; +NaOMe 245, 272, 304sh, 362sh, 418; + NaOAc 265, 319sh, 362, 396; +NaOAc–H_3BO_3 264, 316sh 362. IR ν_{max}^{KBr} cm^{-1}. 3440 (OH), 1650 (C=O), 2950 (C–H), 1620 (C=C), 1120–1000 (C–O).

Acid hydrolysis of **1** *and* **2**. The glycosides, **1** and **2** in 2 M HCl–MeOH (5 ml) were refluxed for 2 hr, H_2O added and the mixture extracted with EtOAc. The aqueous layer was neutralized with Ag_2CO_3, the ppt. filtered and the filtrate evapd to give a residue.

Identification of sugars and aglycone. The neutral aqueous hydrolysates of **1** and **2** were silylated with TMCS and HMDS in pyridine and subjected to GLC (2% OV-1, column temp. 150–250°, 10 min, dect. temp. 300°, N_2, 50 ml min^{-1}) along with silyl derivatives of standard sugars (R_t 3.9, 3.8 min for rhamnose; 3.9, 4.5 min for xylose). The aglycones in the EtOAc fraction were cryst. from $CHCl_3$–MeOH as yellow needles, mp 280–281° and identified as kaempferol by spectral and chromatographic comparison with an authentic sample. Found C 62.80, H 3.44. $C_{15}H_{10}O_6$ requires C 62.93, H 3.49%. UV λ_{max}^{MeOH} cm^{-1}: 249sh, 265, 295sh, 320sh, 370; $+AlCl_3$ 259sh, 266, 300sh, 364, 421; $+AlCl_3$–HCl 256sh, 265, 301sh, 364, 422; +NaOMe 260sh, 282, 315, 430; +NaOAc 277, 300, 398.

Acetylation of **2**. Compound **2** was acetylated and purified as described for **1**. ^1H NMR ($CDCl_3$)δ: 7.88 (2H, *d*, $J=9$ Hz, H-2′,6′), 7.28 (2H, *d*, $J=9$ Hz, H-3′,5′), 7.08 (1H, *d*, $J=2.4$ Hz, H-8), 6.78 (1H, *d*, $J=2.4$ Hz, H-6), 5.19 (1H, *d*, $J=8.3$ Hz, H-1 Xyl), 5.63 (1H, *d*, $J=1$ Hz, H-1 Rham), 1.23 3H, *d*, $J=6.1$ Hz, Rham-Me), 3.78–5.63 (10H, *m*, Gly-H), 2.4 (3H, *s*, OAc-5), 2.34 (3H, *s*, OAc-4′), 1.98–2.20 (18H, *m*, aliphatic MeCO). MS EIMS (70 eV) *m/z* 642 $[M-\text{acetylated pentose}+H]^{+\cdot}$, 628 $[M-\text{acetylated hexose}+H]^{+\cdot}$, 600 $[M-\text{acetylated pentose}-Ac+H^+]^{+\cdot}$, 558 $[M-\text{acetylated pentose}+H-2\times Ac]^{+\cdot}$, 586 $[M-\text{acetylated hexose}+H^+-Ac]^+$, 370 $[M-\text{acetylated pentose}-\text{acetylated hexose}+2H]^{+\cdot}$, 286 $[M-614]^{+\cdot}$, 273 $[(Rham)Ac_3]^+$, 259 $[(Xyl)Ac_3]^+$, 153 $[A_1+H]^+$, 121 $[B_2]^+$.

Enzymatic hydrolysis of **2**. Hydrolysis of **2** with β-xylosidase was carried out under the same conditions as **1** to obtain the same products.

Acknowledgements—The authors thank Prof. S. A. A. Zaidi (Chairman, Department of Chemistry, Aligarh Muslim University, Aligarh) for the provision of facilities. One of us (NJ) thanks the CSIR, New Delhi for a senior research fellowship.

REFERENCES

1. Vasishta, P. C. (1989) *Taxonomy of Angiosperms*, pp. 648–652. Ramchand.
2. Crawford, D. J. (1975) *Brittonica* **27**, 279.
3. Arasawa, M., Minabe, N., Saeki, R., Takakuwa, T. and Nakaoki, T. (1971) *Yakugaku Zasshi* **91**, 522.
4. Crawford, D. J. and Evans, K. A. (1978) *Brittonica* **30**, 313.
5. Crawford, D. J. and Mabry, T. J. (1978) *Biochem. Syst. Ecol.* **6**, 189.
6. Mandich, L. M., Barros, C. and Silva, M. J. (1982) *Bol. Soc. Chil. Quim.* **27**, 175.
7. Marby, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids*. Springer, New York.
8. Markham, K. R. and Marby, T. J. (1975) in *The Flavonoids* (Harborne, J. B., Mabry, T. J. and Mabry, H., eds), pp. 48–63. Chapman and Hall, London.
9. King, F. E., Clark-Lewis, J. W. and (in part) Forbes, W. F. (1955) *J. Chem. Soc.* 2948.
10. King, F. E. and King A. (1950) *J. Chem. Soc.* 168.
11. Petek, F. (1965) *Bull. Soc. Chim. Fr.* 263.

Phytochemistry, Vol. 29, No. 12, pp. 3991–3992, 1990
Printed in Great Britain.

0031-9422/90 $3.00+0.00

A MOSKACHAN FROM ROOTS OF *RUTA CHALEPENSIS*

A. ULUBELEN and N. TAN

Faculty of Pharmacy, University of Istanbul, Istanbul, Turkey

(*Received in revised form* 18 *April* 1990)

Key Word Index—*Ruta chalepensis*; Rutaceae; roots; alkaloids; coumarins; moskachans; chalepimoskachan.

Abstract—In addition to previously obtained coumarins and alkaloids, a group of additional coumarins, xanthatoxin, bergapten and rutolide as well as alkaloids graveolinine, 1-hydroxy-*N*-methylacridone and two moskachans B and D together with the new moskachan, chalepimoskachan were isolated from a new collection of the roots of *Ruta chalepensis*.

INTRODUCTION

In order to isolate antifertility compounds aerial parts [1] and roots [2] of *Ruta chalepensis* have been studied and coumarins as well as alkaloids were obtained which did not exhibit the expected activity. In the present study on a new collection of roots of this species additional coumarins, xanthotoxin, bergapten [1], rutolide [3], and alkaloids, graveolinine, 1-hydroxy-*N*-methylacridone [4], and shikimic acid derivatives moskachan B and D [5] were isolated together with a new moskachan, chalepimoskachan (**1**), in addition to the compounds already obtained