was chromatographed on a Si gel column with a $CHCl_3$–MeOH gradient, collecting those fractions which gave a positive HCl–Mg reaction. These fractions were chromatographed on a Si gel column with $CHCl_3$–MeOH (13:7) to give a yellow powder (**1a**).

3-O-(2^G-Rhamnosylrutinosyl)-7-O-β-glucosylquercetin (**1a**). 60 mg (from abs. MeOH), mp 197–203°, R_f 0.17 on TLC, EtOAc-MeCOEt-HCOOH–H_2O (5:3:1:1) 269 (sh), 357; +$AlCl_3$: 274, 300 (sh), 411.5; +$AlCl_3$/HCl: 270, 300 (sh), 402; +NaOAc: 261.5, 294 (sh), 378, 430 (sh); +NaOMe: 245 (sh), 267, 396.5. IR: KBr—3380 (OH) 2920 (CH), 1660 (C=O), 1600 (C=C), 1200, 1070 (C—O) (Found: C, 48.56; H, 5.61. $C_{39}H_{50}O_{25}\cdot 2\frac{1}{2}H_2O$, requires: C 48.60; H, 5.75%).

3-O-(2^G-Rhamnosylrutinosyl)-7-O-β-glucosylquercetin peracetate (**1b**). **1a** was treated with Ac_2O and C_4H_5N at room temp. for 7 days to give the acetate (**1b**). ^1H NMR (60 MHz, $CDCl_3$): δ 0.85–1.10 (6H, *m*, rhamnose-$CH_3\times 2$) 1.19–2.16 (36H, *m*, glycose-$COCH_3\times 12$), 2.30, 2.35, 2.50 (9H, each *s*, 5, 3′, 4′-$OCOCH_3\times 3$), 3.45–5.70 (30H, *m* glycose-H), 6.70 (1H, *d*, $J=3$ Hz, 6-H), 7.03 (1H, *d*, $J=3$ Hz, 8-H), 7.35 (1H, *br*, 5′-H), 7.93–8.03 (2H, *m*, 2′,6-H) MS *m/e* (rel. int.): 791, 759, 717, 519 (2.3), 428 (1.0) 386 (4.7), 344 (11.0), 331 (38.0), 302 (20.6), 273 (100) 213 (16.5), 169 (78.0), 153 (51.2), 139 (13.1), 111 (34.5) 109 (31.1).

Enzymatic hydrolysis of **1a**. **1a** was treated with β-glucosidase (Miles laboratories) at room temp. for 2 weeks, 3-O-(2^G-rhamnosylrutinosyl)quercetin (R_f 0.30) was identified by TLC (EtOAc–MeCOEt–HCOOH–H_2O, 5:3:1:1, with an authentic sample. D-glucose was identified by GLC.

REFERENCES

1. Sakushima, A., Nishibe, S., Hisada, S., Nro, Y. and Hisada, Y. (1976) *Yakugaku Zasshi* **96,** 1046.
2. Part of this work was presented at the 24th Annual Meeting of the Japanese Society of Pharmacognosy, Tokyo, September, 1977.
3. Mabry, T. J., Markham, K., R. and Thomas, M. B. (1970) *The Systematic Identification of the Flavonoids*. Springer, Berlin.
4. Harborne, J. B., Mabry, T. J. and Mabry, H. (1975) *The Flavonoids*. Chapman & Hall, London.
5. Komori, T., Ida, Y., Mutou, Y., Miyahara, K., Nohara, T. and Kawasaki, T. (1975) *Biomed. Mass Spectrom.* **2,** 65.
6. Ogawa, M. and Ogihara, Y. (1975) *Yakugaku Zasshi* **95,** 655.

Phytochemistry, 1980, Vol. 19, pp. 713–714. Pergamon Press Ltd. Printed in England.

QUERCETAGETIN 5-METHYL ETHER FROM THE PETALS OF *TAGETES PATULA*

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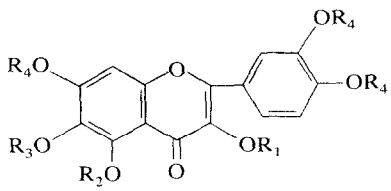
Tagetes patula has been examined extensively for its chemical components [1]. The present communication describes the isolation and characterization of a new flavone, allopatuletin, from the petals. Air-dried petals (4 kg) of *T. patula* were extracted successively with petrol, C_6H_6 and EtOH. The EtOH extract was extracted with Et_2O and then EtOAc to separate the glycosidic and non-glycosidic fractions. The glycosidic fractions (Et_2O and EtOAc insoluble) yielded patulitrin and quercetagitrin.

The non-glycosidic fraction was chromatographed over a Si gel column using several solvent systems. Elutions with C_6H_6–MeOH (93:7; 9:1) gave compounds A and B, C_6H_6–MeOH (17:3; 41:9) yielded compounds C and D whereas C_6H_6–MeOH (7:3) gave D only. Since these mixtures could not be further resolved by column chromatography the fractions A+B and C+D were acetylated (Ac_2O/Py) separately and the resulting acetate mixtures (A_1+B_1 and C_1+D_1) were separated and isolated by PLC on Si gel (C_6H_6–MeOH; 9:1). A_1–D_1 were deacetylated to obtain A–D using EtOH–HCl (19:1) at 100° for 30 min. On direct comparison with authentic samples, A, B, D and their acetates were identified as luteolin, patuletin, quercetagetin and their acetates, respectively (mp, mmp, TLC, UV, NMR and co-IR). C, a new flavone, allopatuletin was characterized as 3,6,7,3′,4′-pentahydroxy-5-methoxyflavone (**1**).

Allopatuletin (**1**) analysed for $C_{16}H_{12}O_8$, gave a pentamethyl ether (**1a**), a pentaacetate (**1b**), a pentaethyl ether (**1c**) and positive ferric and Mg/HCl tests. Colour reactions, spectral (IR and UV) data and derivatives indicated **1** to be a pentahydroxy flavone. Moreover, the acetate (**1b**) was shown by its NMR



1 $R_1 = R_3 = R_4 = H$; $R_2 = Me$
1a $R_1 = R_2 = R_3 = R_4 = Me$
1b $R_1 = R_3 = R_4 = COMe$; $R_2 = Me$
1c $R_1 = R_3 = R_4 = Et$; $R_2 = Me$
1d $R_1 = R_2 = R_3 = R_4 = H$
1e $R_1 = R_3 = R_4 = Et$; $R_2 = H$
2 $R_1 = R_2 = R_4 = H$; $R_3 = Me$
3 $R_1 = Me$; $R_2 = R_3 = R_4 = H$

spectrum to have five OAc (δ 2.33–2.43; 15H), one OMe (δ 3.94, 3H) and the 3,5,6,7,3′,4′-hexaoxygenation pattern was also confirmed by the identity of methyl ether of **1** with synthetic quercetagetin hexamethyl ether (**1a**). **1** was, thus, considered to be a quercetagetin monomethyl ether. As on direct comparison, **1** was found to be different from patuletin (**2**), it was named allopatuletin. In allopatuletin, the OMe is placed at C-5 and the five hydroxyl substituents are located at other positions. This conclusion was based on the following considerations: (a) allopatuletin (**1**) gave protocatechuic acid on alkali degradation fixing two hydroxyl groups at C-3′ and C-4′, (b) it did not give a positive Asahina–Inubuse test [2, 3] and also had a mp markedly different from quercetagetin 3-methyl ether (**3**) [4] indicating an OH instead of OMe at C-3, (c) it was different from patuletin (**2**) suggesting an OH at C-6, (d) it was soluble in aq. Na_2CO_3 and also gave UV shifts with NaOAc, showing a free OH at C-7, and (e) unlike polyhydroxyflavones with a free OH at C-5, it underwent methylation with CH_2N_2 in Et_2O to yield **1a** and with Et_2SO_4/K_2CO_3 in Me_2CO readily (10 hr) gave **1e** thereby ruling out the presence of a chelated OH at C-5. *A priori*, allopatuletin is considered to be quercetagetin 5-methyl ether (**1**) which is supported by the identity of its pentaethyl ether with the synthetic 3,6,7,3′,4′-pentaethoxy-5-methoxyflavone (**1c**) obtained by the ethylation of quercetagetin (**1d**) followed by the methylation of the resulting pentaethyl ether (**1e**). This conclusion was further confirmed by the synthesis of allopatuletin [5].

EXPERIMENTAL

Allopatuletin (**1**) gave yellow crystals (50 mg) from EtOH; mp 234–236°; positive ferric and Mg/HCl tests but negative Asahina–Inubuse test [2, 3] (Found: C, 57.40; H, 3.9. $C_{16}H_{12}O_8$ requires: C, 57.83; H, 3.64%). UV (MeOH) nm: 260, 355; +$AlCl_3$: 270, 395; +$AlCl_3$ + HCl: 265, 390; +NaOAc: 250, 285, 400 nm; +NaOAc+H_3BO_3: 270, 285, 400. IR (KBr) cm^{-1} 3350 (hydroxyl), 1670 (conjugated carbonyl). On alkali degradation it yielded protocatechuic acid and on methylation with CH_2N_2 in Et_2O gave a methyl ether, colourless needles from $CHCl_3$–petrol, mp 142–143°, identical with synthetic quercetagetin hexamethyl ether (**1a**). Acetylation (Ac_2O/Py) of **1** gave **1b**, colourless crystals from EtOAc–petrol; mp 215–216° (Found: C, 57.40; H, 4.4. $C_{26}H_{22}O_{13}$ requires: C, 57.56; H, 4.59%). ^1H NMR: ($CDCl_3$, TMS as the int. standard): δ 2.33–2.43 (15H, 5×O—CO—Me), 3.94 (3H, OMe), 6.94 (1H, C-8—H), 7.42 (1H, C-5′—H), 7.69 (2H, C-2′—H and C-6′—H). Ethylation of **1** in Me_2CO by refluxing for 10 hr with Et_2SO_4 (5 mol)/K_2CO_3 gave **1c**, colourless needles from MeOH, mp 125–126° (Found: C, 65.70; H, 7.2. $C_{26}H_{32}O_8$ requires: C, 66.08; H, 6.83%), identical with the synthetic cpd.

3,6,7,3′,4′-*Pentaethoxy-5-hydroxyflavone* (**1e**). Quercetagetin (**1d**) (0.2 g), Et_2SO_4 (0.43 ml), K_2CO_3 (2 g) and Me_2CO (100 ml) were refluxed for 10 hr and the reaction product worked up giving **1e**, which cryst. from MeOH as light yellow needles (0.12 g), mp 136–137°, positive ferric reaction (Found: C, 65.30; H, 6.70. $C_{25}H_{30}O_8$ requires: C, 65.49; H, 6.60%).

3,6,7,3′,4′-*Pentaethoxy-5-methoxyflavone* (**1c**). A mixture of **1e** (0.1 g), Me_2SO_4 (0.025 ml), K_2CO_3 (1 g) and Me_2CO (60 ml) was refluxed for 24 hr and the resulting methylated product worked up. 3,6,7,3′,4′-Pentaethoxy-5-methoxyflavone (**1c**) cryst. from MeOH as colourless needles (0.07 g), negative ferric reaction, mp 125–126° (Found: C, 65.8; H, 7.0. $C_{26}H_{32}O_8$ requires: C, 66.08; H, 6.83%). **1c** was identical with the ethyl ether of **1**.

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REFERENCES

1. Rodríguez, E. and Mabry, T. J. (1977) in *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds.) pp. 786–797. Academic Press, London.
2. Asahina, Y. and Inubuse, M. (1928) *Ber. Dtsch. Chem. Ges.* **61**, 1646.
3. Asahina, Y. and Inubuse, M. (1931) *Ber. Dtsch. Chem. Ges.* **64**, 1256.
4. Bohm, B. A., Collins, F. W. and Bose, R. (1977) *Phytochemistry* **16**, 1205.
5. Bhardwaj, D. K., Jain, R. K., Mehta, C. K. and Sharma, G. C. (1980) *Curr. Sci.* **49** (in press).