Säulenchromatographie (Sigel Akt. St. II) und weiter durch PLC (Sigel GF 254). Als Laufmittel dienten Et_2O–PÄ-Gemische. Die isolierten Substanzen sind in der Reihenfolge ihrer Polarität angegeben. Bereits bekannte Substanzen identifizierte man durch Vergleich der UV-, IR- und NMR-Spektren.

Felicia wrightii *Hilliard et Burtt.* 120 g Wurzeln ergaben 20 mg (1) und 3 mg (2) (Et_2O–PÄ 1:3). 400 g oberirdische Teile lieferten 3 mg (3) (Et_2O–PÄ 1:10) und 3 mg (1).

Felicia uliginosa (*Wood et Evans*) *Gray*. 200 g Wurzeln ergaben 10 mg (4) und 200 g oberirdische Teile 3 mg (5) Et_2O–PÄ 1:10).

3-Propyl-isocumarin (2). Farbloses Öl, *IR*. CO 1745; C=C 1660 cm^{-1}. UV: $\lambda_{max} = 320, 277, 266$ nm ($\epsilon = 3700, 9000, 10600$). MS: M^+ *m/e* 188.085 (100%) (ber. für $C_{12}H_{12}O_2$ 188.084).

Eugenol-isovalerat (3). Farbloses Öl *IR*. COOR 1740; $CH=CH_2$ 920 cm^{-1}. *MS*. M^+ *m/e* 248.142 (17%) (ber. für $C_{15}H_{20}O_3$ 248.141); $-O=C=CH\ CH\ (Me)_2$ 164 (100).

Tetradeca-5.7.9.11-tetraen-säuremethylester (5). Farbloses Öl, *IR*. CO_2R 1735; $(CH=CH)_4$ (trans) 990 cm^{-1}. UV: $\lambda_{max} = 318, 303, 289$ nm ($\epsilon = 48000, 52700, 34200$). MS: M^+ *m/e* 234.162 (100%) (ber. für $C_{15}H_{22}O_2$ 234.162); $-CH_2CH_2$-CO_5Me 147 (41).

Anerkennung—Herrn Prof. Dr. J. Grau danken wir für das Pflanzenmaterial, der Deutschen Forschungsgemeinschaft für die Unterstützung dieser Arbeit.

LITERATUR

1. Bohlmann, F., Burkhardt, T. und Zdero, C. (1975) *Naturally Ocurring Acetylenes*, Academic Press, New York.
2. Bohlmann, F. und Zdero, C. (1969) *Chem. Ber.* **102**, 1691.
3. Prof. Dr. J. Grau, Privatmitteil.

Phytochemistry, 1976, Vol. 15, pp. 1319–1320. Pergamon Press. Printed in England.

HERATOMIN AND HERATOMOL, NEW COUMARINS FROM *HERACLEUM THOMSONI*

Bishan D. Gupta, Sunil K. Banerjee, K. L. Handa and C. K. Atal
Regional Research Laboratory (C.S.I.R.), Jammu-Tawi, India

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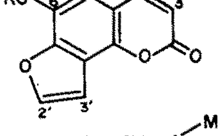
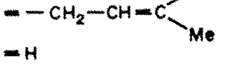
Key Word Index—*Heracleum thomsoni*; Umbelliferae; furanocoumarins; heratomin; heratomol; 6-(3-methylbut-2-enyloxy)angelicin; 6-hydroxyangelicin; lanatin; isobergapten; isoimperatorin; imperatorin.

In continuing our research [1–2] on the genus *Heracleum*, we encountered *Heracleum thomsoni*, a species growing in Ladakh, India. We have isolated a number of coumarins from the roots of this plant two of which, heratomin and heratomol, are new and assign them the structures (1) and (2) on the basis of following evidence.

The petrol ether extract of *H. thomsoni* on chromatography yielded lanatin (3), isobergapten, isoimperatorin, imperatorin and heratomin (1). This is the second report on the occurrence of lanatin in nature. Heratomin (1), mp 110–111°, has the molecular formula $C_{16}H_{14}O_4$ (M^+ 270). In the IR it shows characteristic absorption of a furanocoumarin at 1716, 1637, 1586, 878 and 753 cm^{-1}. The NMR spectrum (60 MHz) shows signals for an isopentenyl aromatic ether group (see Experimental). This is substantiated by the presence in the MS of an intense peak at *m/e* 201 ($M^+ - 69$, for isopentenyl). H-3, H-4 and H-5 appeared in the NMR spectrum at δ 6.32, 7.72 and 6.88 respectively while H-3′ and H-2′ showed up at 7.06 and 7.65 respectively. Heratomin was readily dealkylated with ethanolic HCl to give a phenol, $C_{11}H_6O_4$ (M^+ 202) which was characterized as 6-hydroxyangelicin (2) as this on methylation with diazomethane yielded sphondin (3). The above data establish the structure of heratomin (1) as the isopentenyl ether of 6-hydroxyangelicin, i.e. 6-(3-methylbut-2-enyloxy) angelicin.



(1)

R = $-CH_2-CH=C(Me)_2$

(2) R = H

(3) R = Me

Heratomol (2), $C_{11}H_6O_4$, (M^+ 202), mp 253–254°, isolated from the benzene extract of the roots on methylation with diazomethane yielded sphondin (3). Therefore, heratomol (2) is 6-hydroxyangelicin, the dealkylated product of heratomin.

EXPERIMENTAL

Mp's are uncorrected. The 60-MHz NMR spectra were recorded in $CDCl_3$ with TMS (δ 0.00) as internal standard.

Isolation of heratomin and heratomol. Dried powdered roots (2 kg) of *H. thomsoni* (Voucher specimen No. 12684/75 deposited at Plant Survey Division, R.R.L.) were soxhletted successively with petrol (60–80°) and C_6H_6. The brown residue (60 g) left after removal of petrol was chromatographed over acidic alumina (grade IV, 1.5 kg). Elution with petrol gave successively lanatin, mp 140–141° (1 g), isobergapten, isoimperatorin, imperatorin and heratomin (2.0 g). The C_6H_6 extract was chromatographed on Si gel. C_6H_6 eluate gave heratomin (0.1 g). $CHCl_3$ eluate yielded heratomol (0.4 g). The known compounds were identified by their mp's, TLC, IR, NMR and MS.

Heratomin, from Me_2CO–petrol as colourless needles, mp 110–111°. Found: C, 70.6; H, 4.9. $C_{16}H_{14}O_4$ requires: C, 71.1; H, 5.2%. R_f 0.60 [Si gel, C_6H_6–Me_2 CO (9:1)]. This on Si gel gives a light blue fluorescence under UV. ν_{max}^{KBr} (cm^{-1}): 1716 (coumarin lactone CO), 1637 (3,4-double bond in conjugation with CO), 1260 (ether), 1586, 878 (furan ring peak due to out-of-plane deformation vibration of C-H) and 753 (C-H in-plane deformation vibration in furanocoumarin). NMR (δ in ppm): 1.79 (6H, *s*, methyls), 4.73 (2H, *d*, *J* 7 Hz, Ar–O–$\underline{CH_2}$–CH=), 5.59 (1H, coupled *t*, *J* 7 Hz,–O–CH$_2$–$\underline{CH}$=), 6.32 (1H, *d*, *J* 9.5 Hz, H-3), 7.72 (1H, *d*, *J* 9.5 Hz, H-4), 6.88 (1H, *s*, H-5), 7.06 (1H, *d*, *J* 2 Hz, H-3'), 7.65 (1H, *d*, *J* 2 Hz, H-2').

Dealkylation of heratomin. Heratomin (200 mg) was heated under reflux with 4% HCl in EtOH (20 ml) for 30 min. The mixture was diluted with H_2O (80 ml) and the solid, which separated, crystallized from EtOH to yield phenol (**2**), as needles, mp 253–254° (M$^+$ 202). (Found: C, 64.9; H, 2.8. $C_{11}H_6O_4$ requires: C, 65.3; H, 3.0%).

Methylation of phenol (**2**). A solution of phenol (50 mg) in MeOH (10 ml) was treated with an ethereal solution of CH_2N_2. After 24 hr the solvent was evaporated and the residue crystallized from Me_2CO–petrol giving sphondin as needles, mp 191–192° (mmp, superimposable IR, NMR, MS, Co-TLC).

Heratomol. It crystallized from MeOH, as needles, mp 253–255°. Found: C, 64.8; H, 2.9. $C_{11}H_6O_4$ requires C, 65.3; H, 3.0%. M$^+$ 202. It did not depress the mp of 6-hydroxyangelicin (2) (the dealkylated product of heratomin). R_f 0.20 [Si gel, C_6H_6–Me_2 CO (9:1)]. On Si gel this gives a light blue fluorescence under UV.

Methylation of heratomol. It was methylated in the usual way with CH_2N_2. The methyl ether, mp 192–193°, was found to be identical with sphondin (mmp, Co-TLC, IR, NMR, MS).

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REFERENCES

1. Gupta, B. D., Banerjee, S. K. and Handa, K. L. (1975) *Phytochemistry* **14**, 2533.
2. Gupta, B. D., Banerjee, S. K. and Handa, K. L. *Phytochemistry* (in Press).
3. Steck, W. and Mazurek, M. (1972) *Lloydia* **35**, 418.

Phytochemistry, 1976, Vol. 15, pp 1320–1321 Pergamon Press Printed in England.

THE SYNTHESIS OF AFZELIN, PAEONOSIDE AND KAEMPFEROL 3-*O*-β-RUTINOSIDE

BORBÁLA VERMES,* LORAND FARKAS,* MIHÁLY NÓGRÁDI,*
HILDEBERT WAGNER† and RICHARD DIRSCHERL†
*Institute for Organic Chemistry, Technical University H-1521 Budapest, P.O.B. 91, Hungary;
†Institut für pharmazeutische Arzneimittellehre der Universität München, Deutschland

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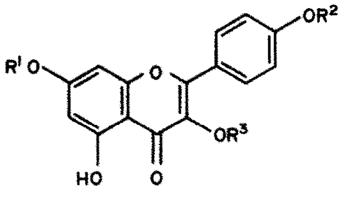
Key Word Index—Kaempferol glycosides; synthesis; afzelin; paeonoside.

Abstract—The structure of afzelin (kaempferol 3-*O*-α-L-rhamnopyranoside) and paeonoside (kaempferol 3,7-bis-*O*-β-D-glucopyranoside) has been confirmed by total synthesis. Synthetic kaempferol 3-*O*-β-rutinoside had a mp of 190–192° suggesting that those natural kaempferol 3-*O*-rhamnoglucosides which melt in the same range are also 3-*O*-β-rutinosides.

In this paper we report the unambigous synthesis of three kaempferol glycosides with the purpose of supporting thereby the structures of the corresponding natural products.

The isolation of afzelin, a kaempferol 3-*O*-rhamnoside has been reported from at least nine different sources, the first being in 1950 by King and Acheson from an *Afzelia* sp. [1]. Due to their quite similar mp's (mainly 172–174°) it has been generally assumed that these rhamnosides are identical and except in two cases [2,3], it has been assumed that the sugar moiety is in the α-pyranoside form (**1**). For substances isolated from *Aesculus hippocastanum* [2] and *Galega officinalis* [3], rhamnofuranoside structures were postulated.

We prepared **1** by coupling 7,4'-di-*O*-benzylkaempferol (**2**) [4] with α-benzoyl-bromorhamnose [5] to give, after saponification, the dibenzyl ether (**3**), which was converted to kaempferol 3-*O*-α-L-rhamnopyranoside (**1**), mp



(**1**) R^1 = R^2 = H, R^3 = α-L-Rha
(**2**) R^1 = R^2 = CH$_2$Ph, R^3 = H
(**3**) R^1 = R^2 = CH$_2$Ph, R^3 = α-L-Rha
(**4**) R^1 = R^3 = β-D-Glc, R^3 = H
(**5**) R^1 = R^3 = H, R^2 = CH$_2$Ph
(**6**) R^1 = R^3 = β-D-Glc R^2=CH$_2$Ph
(**7**) R^1 = R^2 = H, R^3 = β-rutinosyl
(**8**) R^1 = R^2 = CH$_2$Ph, R^3 = β-rutinosyl

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‡ Kaempferol 3-*O*-(3-*O*-α-L-rhamnopyranosyl-β-D-glucopyranoside) from *Rungia repens*; the disaccharide is called rungiose.