5. Cheng, K. P., Nagano, H., Bang, L. and Ourisson, G. (1977) *J. Chem. Res.* (S) 217; *J. Chem. Res.* (M) 2501.
6. Nagano, H., Poyser, J. P., Cheng, K. P., Bang, L. and Ourisson, G. (1977) *J. Chem. Res.* (S) 218, *J. Chem. Res.* (M) 2522.
7. Van Lier, J. E. and Smith, L. L. (1970) *J. Org. Chem.* **35**, 2627.
8. Teng, T. J., Kulig, M. J., Smith, L. L. and Kang, G. (1973) *J. Org. Chem.* **38**, 119.
9. Katsui, N., Matsue, H., Hirata, T. and Masamune, T. (1972) *Bull. Chem. Soc. Jpn* **45**, 223.
10. Rohmer, M. and Brandt, R. (1973) *Eur. J. Biochem.* **36**, 446.
11. Rohmer, M., Ourisson, G., Benveniste, P. and Bimpson, T. (1975) *Phytochemistry* **14**, 727.
12. Schroeder, G., Rohmer, M., Beck, J. P. and Anton, R. (1979) *Planta Med.* **35**, 235.

Phytochemistry, 1980, Vol. 19, pp. 2215–2216. © Pergamon Press Ltd. Printed in England. 0031 9422/80/1001-2215 $02.00/0

A PHENOLIC GLUCOSIDE FROM THE SEEDS OF *CARUM COPTICUM*

S. K. GARG, N. D. SHARMA and S. R. GUPTA

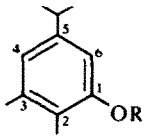
Department of Chemistry, University of Delhi, Delhi-110007, India

(*Received* 28 *January* 1980)

Key Word Index—*Carum copticum*; Umbelliferae; phenolic glucoside; 2-methyl-3-glucosyoxy-5-isopropylphenol; structure elucidation.

A continuation of our study of Indian medicinal plants [1, 2] has led to a chemical investigation of the seeds of *Carum copticum* and the isolation of a new phenolic glucoside, 2-methyl-3-O-β-D-glucosyloxy-5-isopropylphenol (**1**). *C. coptium* is cultivated both in the Mediterranean region and India and is known for its medicinal properties [3].

1, mp 177–8°, M$^+$ 328, was obtained as a colourless powder. The spectral studies of **1** and its acetate, **2** showed the presence of two protons, a hydroxyl, a glucosyl, a methyl and an isopropyl group substituted in a benzene ring. A positive Gibb's test of **1** and of its acid hydrolysed methyl ether, **4** indicated that the glucosyloxy group is *meta* to the phenolic hydroxyl. If the glucosyloxy group was *ortho* to the hydroxyl, the two protons would appear as doublets of J = 10 Hz each. The appearance of two singlets at δ 6.82 (1 H) and δ 7.0 (1 H) confirms the presence of a glucosyloxy group at the 3-position in the phenol nucleus leaving positions 2 and 5 for the methyl and isopropyl groups. The possibility of an isopropyl group at position 2 was ruled out by direct comparison of the derivative **6** (see Experimental) with an authentic sample of thymol (2-isopropyl-5-methylphenol) methyl ether. Permethylation [5] and hydrolysis of **1** gave 2,3,4,6-tetra-*O*-methyl-D-glucopyranose establishing that C_1 of the glucose is linked with the aglucone, **3**. Finally, the β-linkage of the glucose was confirmed by enzymatic hydrolysis.



1 R = H, R_1 = OGlc.
2 R = Ac, R_1 = −OGlc·Ac_4
3 R = H, R_1 = −OH
4 R = Me, R_1 = OH
5 R = Me, R_1 = −O·SO_2·C_6H_4·Me−*p*
6 R = Me, R_1 = H

EXPERIMENTAL

UV spectra were recorded in MeOH and in the NMR spectra TMS was used as internal standard.

Extraction and Isolation. Dried *C. copticum* seeds (3.0 kg) were extracted successively with petrol, C_6H_6 and EtOH. The C_6H_6 insoluble portion of the EtOH extract was concd and chromatographed on a Si gel column (400 g) with a $CHCl_3$ → MeOH gradient. The fractions eluted with $CHCl_3$–MeOH (23:2) on prep. TLC (Si gel, EtOAc–MeOH–H_2O, 100:16.5:13.5) yielded the glucoside, **1** (500 mg).

Identification of **1** R_f s on Si gel: 0.43 (EtOAc–MeOH–H_2O, 100:16.5:13.5); 0.55 ($CHCl_3$–MeOH, 7:3); (Found: C, 58.2; H, 7.7.

$C_{16}H_{24}O_7$ requires: C, 58.5; H, 7.7%); UV λ_{max} nm (log ε): 260 (3.41), 275 (3.59) and 320 (3.14); IR(KBr) ν cm^{-1}: 3378, 1510, 1452, 1371, 1253, 1060 and 822; MS *m/e* (% abundance): 328 (M^+, 2), 194 (3), 167 (13), 166 (100), 151 (31), 137 (3), 91 (5) and 73 (8). It gave positive Molisch's and Gibb's tests. Acetate **2**(Ac_2O/Pyridine), colourless powder from EtOAc–petrol, mp 106–107°; UV λ_{max} nm: 265, 275 and 320; IR(KBr) ν cm^{-1} 1743, 1500, 1370, 1216, 1038 and 912; ^{1}H NMR($CDCl_3$): δ 1.20 and 1.29 (*s*, 3 H) each, gem diMe), 2.10 (*brs*, 12 H, 4 × –OCOMe), 2.18 (*s*, 3 H, –OCOMe), 2.34 (*s*, 3 H, Me), 3.0 (*t*, 1 H, → CH), 3.80–4.32 (*m*, 3 H, sugar protons), 4.93–5.41 (*m*, 4 H, sugar protons), 6.82 and 7.0 (*s*, 1 H each, H_6 and H_4).

1 (50 mg) was hydrolysed with H_2SO_4 (7%) for 4 hr. under reflux. The soln was extracted with EtOAc and D-glucose was detected in the aq. soln. The EtOAc extract on evapn gave the aglucone, **3**, as a light brown semi-solid, UV λ_{max} nm: 275 and 310; IR(KBr) ν cm^{-1}: 3418, 1630, 1460, 1379, 1140 and 1090. **1** (250 mg) was methylated with Me_2SO_4–K_2CO_3–Me_2CO for 30 hr and the methyl ether hydrolysed with H_2SO_4 (7%). The aglycone was extracted with Et_2O and purified by prep. TLC (Si gel, EtOAc–C_6H_6, 1:49), when it was obtained as a dark brown semi-solid, **4** M^+ 180; UV λ_{max} nm: 285; IR(KBr) ν cm^{-1}: 3420, 1610, 1491, 1442, 1338 and 1193; ^{1}H NMR($CDCl_3$): δ 1.12 and 1.20 (*s*, 3 H, gem diMe), 2.20 (*s*, 3 H, –Me), 3.21 (*t*, 1 H, → CH), 3.8 (*s*, 3 H, –OMe) and 6.6 (*s*, 2 H, H_6 and H_4). It gave a positive Gibb's test.

4 (200 mg) was tosylated with *p*-Me·C_6H_4·SO_2Cl–K_2CO_3–Me_2CO for 6 hr, filtered and purified by prep. TLC (Si gel, EtOAc–C_6H_6, 1:200) to yield **5** as a semi-solid, UV λ_{max} nm: 260 and 305; IR (KBr) ν cm^{-1}: 1598, 1503, 1397, 1251, 1091 and 846. A mixture of **5** (120 mg), EtOH (10 ml), HCl (4 ml) and Zn granules (400 mg) [4] was refluxed for 1.5 hr filtered, evapd, cooled, diluted with H_2O, extracted with Et_2O and purified by prep. TLC (Si gel, C_6H_6) to yield **6** as a light brown semi-solid, UV λ_{max} nm: 275 and 305; IR(KBr) ν cm^{-1}: 1614, 1598, 1397, 1250, 1147, 1059 and 812; ^{1}H NMR ($CDCl_3$): δ 0.96 and 1.04 (*s*, 3 H each, gem diMe), 2.35 (*s*, 3 H, Me), 3.14 (*t*, 1 H, → CH), 3.78 (*s*, 3 H, –OMe), 6.53 (*d*, J = 4 Hz, 1 H, H_6), 7.22 (*m*, 1 H, H_4) and 7.47 (*d*, J = 9 Hz, 1 H, H_3). **6** was found to be different from an authentic sample of thymol methyl ether on direct comparison (TLC and IR).

Permethylation of **1** by Hakomori's method followed by acid hydrolysis gave 2,3,4,6-tetra-*O*-methyl-D-glucopyranose which was confirmed by direct comparison with an authentic sample. The β-configuration of the glucose linkage was established by the hydrolysis of **1** with emulsin.

REFERENCES

1. Garg, S. K., Gupta, S. R. and Sharma, N. D. (1979) *Phytochemistry* **18**, 1580.
2. Garg, S. K., Gupta, S. R. and Sharma, N. D. (1980) *Planta Med.* **38**, 186.
3. (1976) *The Wealth of India, Raw Materials* Vol. X, p. 267. CSIR. New Delhi.
4. Ahluwalia, V. K. and Sunita (1977) *Indian J. Chem.* **15b**, 936.
5. Hakomori, S. (1964) *J. Biochem.* **55**, 205.