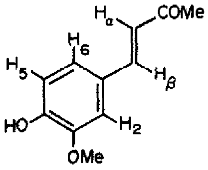
Present work. Further study on the $CHCl_3$ extract of the stems has now yielded emodin, syringaldehyde, syringic acid and dehydrozingerone (**1**). The structures of the first three compounds were determined by spectroscopic data and by comparison with authentic samples. Dehydrozingerone has been never found before in nature, although it was already known as synthetic product.



Scheme 1.

The compounds were separated on a polyamide column and purified on Si gel columns. (**1**), mp 120–124°, showed in the IR spectrum (KBr) bands at ν_{max} 3300 cm^{-1} (OH), 1670 (α,β-unsaturated C=O), 1640 and 970 cm^{-1} (*t*–CH=CH–). The PMR spectrum (60 MHz, $CDCl_3$, TMS) showed the following functional groups: MeCO δ 2.35 (3H, *s*); CH_3O δ 3.92 (3H, *s*); *trans* HC=CH δ 6.60 (1H, *d*, $J_{\alpha\beta}$ 16.0 Hz, H_α) and δ 7.48 (1H, *d*, $J_{\alpha\beta}$ 16.0 Hz, H_β); 1,2,4-trisubstituted benzene δ 6.90 (1H, *d*, J_{5-6} 9.5 Hz, H-5) and δ 7.0–7.2 (2H, *m*, H-2 and H-6). λ_{max}^{EtOH} nm (log ϵ): 240 (3.93), 337 (4.29), which by addition of MeCOONa were shifted to 257 and 406 nm, indicating a free OH group in 4-position. MS (probe, 70 eV, *m/e* rel. int.): 192 M^+ (100); 177 (M^+-15, 95); 145 (71). The structure was finally confirmed by synthesis [2]: condensation of vanillin and acetone in presence of 10% NaOH followed by purification on a Si gel column afforded the 4(4′-hydroxy-3′-methoxyphenyl)3-buten-2-one, mp 128–129° identical with the natural compound in all respects.

It is interesting that some compounds related to (**1**) have been found in other Zingiberaceae: zingerone, gingerols, shogaols and paradols in *Zingiber officinale* Roscoe [3, 4] and in *Amomum melegueta* Roscoe [5, 6]. Dehydrozingerone could arise biogenetically by the condensation of 4-hydroxy-3-methoxycinnamic acid with one malonate unit, followed by double decarboxylation.

REFERENCES

1. Vidari, G., Vita-Finzi, P. and De Bernardi, M. (1971) *Phytochemistry* **10**, 3335.
2. Francesconi, L. and Cusmano, G. (1908) *Gazz. Chim. Ital.* **38** II, 75.
3. Connell, D. W. and Sutherland, M. D. (1969) *Australian J. Chem.* **22**, 1033.
4. Connell, D. W. (1970) *Flavour Ind.* (*London*) **1**, 677.
5. Connell, D. W. (1970) *Australian J. Chem.* **23**, 369.
6. Tackie, A. N., Dwuma-Badu, D., Ayim, J. S. K., Dabra, T. T., Knap, J. E., Slatkin, D. J. and Schiff, P. L., Jr., (1975) *Phytochemistry* **14**, 853.

Phytochemistry, 1976, Vol. 15, p. 1786. Pergamon Press. Printed in England.

1-(3-GLUCOSYLOXY-4-HYDROXYCINNAMYL)GLUCOSE FROM *LANTANA HYBRIDA*

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The presence of 1-caffeylrhamnose in the flowers of *Lantana hybrida* has been reported recently [1]. A new compound (R_f 0.22 in *n*-BuOH–HOAc–H_2O, 4:1:5) was isolated from extracts of the above plant material (collected in Catania, Italy) by preparative PC. The UV spectrum (λ_{max} 335 nm in EtOH) showed a large bathochromic shift (75 nm) in the presence of NaOEt. Controlled acid hydrolysis (10% HOAc; 3.5 hr under reflux) gave D-glucose identified by PC and by the use of glucose oxidase. Methylation with MeI–AgO in $HCONME_2$ [2] followed by acid hydrolysis (0.3 N HCl; 4 hr under reflux) gave 2,3,4,6-tetra-*O*-methyl-D-glucose identified by PC and TLC. Acid hydrolysis (1 N HCl; 0.5 hr at 100°) and treatment with β-glucosidase gave D-glucose and caffeic acid in the ratio of 2.07:1, identified by PC and TLC. Since the compound gave no colour reaction with sodium molybdate [1], the *o*-diphenolic group of caffeic acid is not free. Methylation with CH_2N_2 followed by acid hydrolysis (2 N HCl; 0.5 hr at 100°) gave isoferulic acid identified by PC [3] and TLC; hence the 4-hydroxyl of caffeic acid is free and the 3-hydroxyl is bound by a β-linkage to D-glucose. Since alkaline hydrolysis (0.2 N NaOH; 3 hr at room temp) and treatment with esterase [4] gave D-glucose, this sugar is attached from its 1-position by a β-linkage to the carboxyl group of caffeic acid. The mass spectrum of the permethyl ether showed a parent ion at *m/e* 630 (calc. MW 630). Thus the compound must be 1-[3-(β-D-glucosyloxy),4-hydroxycinnamyl]glucose, which has not previously been reported in plants.

REFERENCES

1. Imperato, F., Di Leo, C. and Trovato, P. (1975) *Phytochemistry* **14**, 2725.
2. Piattelli, M. and Minale, L. (1966) *Ann. Chim.* **56**, 1060.
3. Dunlap, W. J. and Wender, S. H. (1960) *J. Chromatog.* **3**, 505.
4. Harborne, J. B. and Corner, J. J. (1961) *Biochem. J.* **81**, 242.