Thin-layer chromatography of guaiacylpropane monomers, selected lignans and phenolic wood extractives

The extensive nature of wood extractives, ranging from lignin precursors to heartwood end products, necessitates a detailed knowledge of isolated constituents and their chromatographic behaviour. In a current study of western hemlock (*Tsuga heterophylla* (Raf.) Sarg.) a large number of reference compounds were either synthesized or collected and their chromatographic properties determined. Although paper chromatographic data on some of these compounds have been published, no adequate collection of information based on the modern technique of thin-layer chromatography was available.

The compounds listed in Table I were differentiated by means of the thin-layer technique. Three separate developing solvent systems on silica gel G, namely benzene–ethanol (BE) (150:22), benzene–acetone (BA) (3:2) and methanol–chloroform (MC) (3:7) were used in addition to the one developing solvent on microcrystalline cellulose, 2% aqueous acetic acid (AA). Compounds with closely related R_F values usually gave sufficiently different colours after coupling with the diazotized sulphanilic acid (DSA) reagent as to be diagnostic. This was most evident in the detection of α-hydroxy-

TABLE I

Compound No.	*Identification*	*R_F × 100*			*DSA colour on silica gel*[a]	*R_F × 100 AA*	*DSA colour on microcrystalline cellulose*[b]
		BE	*BA*	*MC*			
	R = guaiacyl, R′ = syringyl						
1	R—CO—CO—CH_3 Acetylvanilloyl	47	52	83	Yellow	74	Yellow
2	R—CO—CHOH—CH_3 α-Hydroxy-propiovanillone	30	37	77	Brown	72	Brown
3	R—CHOH—CHOH—CH_3	14	30	84	Yellow-orange	83	Yellow-orange
4	R—CHOH—CHOH—CH_2OH Guaiacylglycerol	02	06	50	Yellow-orange	86	Yellow-orange
5	R—CO—CH_2—CH_3	44	61	85	Red	59	Pink
6	R—CHOH—CH_2—CH_3	30	50	90	Yellow-orange	79	Yellow-orange
7	R—CH_2—CH_2—CH_3	59	70	93	Yellow-brown	Undetected	
8	R—CH_2—CO—CH_3 Guaiacyl acetone	44	60	93	Brown	85	Violet
9	R—CH_2—CHOH—CH_3	29	42	85	Pink	69	Pink-violet
10	R—CO—CH_2—CH_2OH β-Hydroxy-propiovanillone	20	32	77	Brown	65	Pink
11	R—CHOH—CH_2—CH_2OH	10	18	75	Yellow-orange	82	Yellow-orange
12	R—CH_2—CO—CH_2—OH ω-Hydroxyguaiacylacetone	32	43	70	Pink	88	Red

(*continued on p. 321*)

TABLE I (*continued*)

Compound No.	Identification	$R_F \times 100$ BE	$R_F \times 100$ BA	$R_F \times 100$ MC	DSA colour on silica gel[a]	$R_F \times 100$ AA	DSA colour on microcrystalline cellulose[b]
13	R—CO—CH_3 Acetovanillone	39	58	93	Brown	70	Pink
14	R—CHOH—CH_3	31	45	93	Yellow-orange	79	Yellow-orange
15	R—CHO Vanillin	40	59	93	Red	75	Red
16	R—CH_2OH Vanillyl alcohol	35	40	72	Yellow-red	82	Yellow-red
17	R—COOH Vanillic acid	S23[c]	S17	S42	Yellow-orange	37	Yellow-orange
18	R′—CHO Syringaldehyde	S38	40	69	Pink	69	Pink
19	R—CH_2—CH=CH_2 Eugenol	61	67	93	Yellow-brown		Diffused
20	R—CH=CH—CH_3 Isoeugenol	57	65	93	Yellow-brown		Diffused
21	R—CH=CH—CHO Coniferaldehyde	47	55	93	Red-brown	49	Violet
22	R—CH=CH—CH_2OH Coniferyl alcohol	37	40	76	Red-brown	65	Violet
23	R—CH=CH—COOH Ferulic acid	S15	S13	S35	Brown	31	Violet
24	Dehydrodiconiferyl alcohol[1]	25	24	73	Brown	70	Pink
25	α-Conidendrin[2]	51	55	93	Pink-brown	0	Pink
26	β-Conidendrin[2]	48	57	93	Yellow-brown	0	Pink
27	α-Conidendrol[3]	S31	S29	82	Grey-yellow	37	Grey-brown
28	β-Conidendrol[3]	S27	S27	82	Grey-yellow	46	Grey-brown
29	α-Conidendric acid[4]	0	01	S18	Brown	74	Red
30	Matairesinol[2]	49	52	82	Brown	57	Red
31	Hydroxymatairesinol[2]	31	39	92	Yellow-orange	71	Yellow-orange
32	Pinoresinol[2]	47	48	87	Pink-brown	56	Pink
33	Symplocosigenol[2]	48	44	84	Red-brown	55	Pink
34	Lirioresinol A[2]	43	30	94	Pink-brown	53	Pink
35	Symplocosin[2]	04	01	68	Brown	66	Pink
36	Liriodendrin[2]	00	00	44	[d]	front	[e]

[a] Silica gel G according to STAHL with 13 % binder, E. Merck, Darmstadt, Germany.
[b] Microcrystalline cellulose, Avicel, FMC Corporation, Pennsylvania, U.S.A.
[c] S = streaking
[d] Detected by spraying with 10 % sulphuric acid and heating to 100°.
[e] Detected with the sodium periodate–potassium permanganate reagent[5].

guaiacyl derivatives which gave a characteristic yellow-orange colour with the DSA reagent. The expected variation of R_F values inherent in the thin-layer technique was kept at a minimum by using freshly-prepared developing solvents each day.

Functional group differences between ketones and alcohols, as well as differences in degree of hydroxyl substitution, are seen by comparing R_F values of compounds 1–16, Table I, in the solvent systems BE and BA. For example, comparison of the ketone–alcohol pairs 1–3, 5–6, 8–9 and 10–11 shows that in each case the alcohol has the lower R_F value. Also, the trend to lower R_F values for increasing hydroxyl substitution is demonstrated by comparing the guaiacylpropane series, compounds 7, 6, 3 and 4. Information of this kind has proved useful in predicting the structure and degree of hydroxyl substitution in related but unknown compounds from western hemlock sapwood extracts.

The author wishes to express his appreciation for gifts of reference compounds used during this study to Drs. E. ADLER, E. DICKEY, K. FREUDENBERG, J. GARDNER, H. HERGERT and H. IMAMURA. Gifts of the conidendrins and conidendrols from Crown Zellerbach, Chemical Products Division, Camas, Washington, U.S.A. are also acknowledged.

Department of Foresty of Canada, Forest Products Laboratory, Vancouver, B.C. (Canada) G. M. BARTON

1 O. GOLDSCHMID AND H. L. HERGERT, *Tappi*, 44 (1961) 858.
2 W. E. HILLIS, *Wood Extractives*, Academic Press, New York and London, 1962, Chap. 4, p. 159.
3 W. M. HEARON, H. B. LACKEY AND W. W. MOYER, *J. Am. Chem. Soc.*, 73 (1951) 4005.
4 B. HOLMBERG, *Chem. Ber.*, 54 (1921) 2389.
5 R. U. LEMIEUX AND H. F. BAVER, *Anal. Chem.*, 26 (1954) 920.

Received May 16th, 1966