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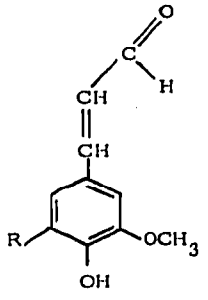
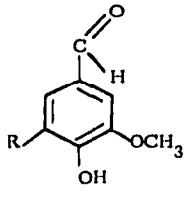
Simple semi-quantitative estimation of sinapyl and certain related aldehydes in wood and in other materials

In the course of an inquiry into the possible aetiological factors of nasopharyngeal tumours among the Chinese and the Kenyans[1], the smoke of Chinese incense and of anti-mosquito coils was tested for known carcinogenic constituents. On thin-layer chromatography a spot was detected which gave a red colour with sulphanilic acid[2]. The compound giving this reaction was identified as sinapyl aldehyde (I)[3]. This is a known constituent of lignins in angiospermous woods[4]. Sinapyl aldehyde was detected in condensates of smoke and in extracts of powdered sandal wood (*Santalum album*) the main constituent of incense, in coconut shell powder (*Cocos nucifera*, the major constituent of anti-mosquito coils) and in a series of hard woods, both in extracts with methanol at room temperature and in condensates obtained by dry distillation[3]. Such preparations contained also coniferyl (II) and syringic (III) aldehydes and vanillin (IV). Furfuraldehyde was obtained on dry distillation, while 3,5-dimethoxy-1,4-benzoquinone was detected in beech extracts.





I R = OCH_3, sinapyl aldehyde

II R = H, coniferyl aldehyde

III R = OCH_3, syringic aldehyde

IV R = H, vanillin

Distillates from gymnospermous woods contained coniferyl aldehyde, vanillin and furfural, but not I or III.

Hard-wood dust came under suspicion also in connection with tumours of the nasal cavities among furniture workers[5]. Sinapyl aldehyde (or its epoxide) may be of interest in this connection. Glycidaldehyde, the epoxide of acrolein, the simplest α,β-unsaturated aldehyde, has been reported to be carcinogenic for mice and for rats[6,7].

In view of the desirability of screening various materials for the content of I and of the other compounds, the micro-distillation method of STAHL[8] was adapted and proved convenient.

About 10–20 mg of the finely powdered material is placed into the wider part of a Pasteur pipette having in the capillary part a constriction and a small bulb. The tube is sealed at the wide end and heated in a horizontal position in a metal block essentially as described by STAHL. The aldehydes sublime into the capillary part of the tube, protruding from the block; the more volatile constituents being absorbed by the water that distills first and acts as a condensing compartment. The block used

TABLE I

R_F VALUES AND COLOUR REACTIONS OF WOOD ALDEHYDES

TLC on Silica Gel G. Solvent system: *n*-hexane–diethyl ether–dichloromethane–glacial acetic acid (4 : 3 : 2 : 1). Spray reagents: A = sulphanilic acid (1 % in 30 % acetic acid); B = 2,4-dinitrophenylhydrazine (0.5 % in 2 *N* HCl); C = phloroglucinol (2.5 % in 3 *N* HCl).

Compound	R_F	*Reagents*		
		A	*B*	*C*
Sinapyl aldehyde	0.35	Red	Orange	Purple
Syringic aldehyde	0.48	Yellow	Orange	Peach
Coniferyl aldehyde	0.56	Orange	Orange	Purple
Vanillin	0.70	Yellow	Orange	Peach
Furfural	0.80	Red	Orange	Grey

had seven cylindrical depressions and allowed six specimens to be heated at the same time and the temperature read on a thermometer. When wood dust is tested, this becomes somewhat charred; the temperature at which the aldehydes come over is about 300° which is maintained for 1.5 h. The capillaries are then eluted with methanol, and appropriate aliquots applied to thin-layer plates (250 μ thick) prepared from Kieselgel G (Merck & Co.), activated at 105° for 90 min. The plates were run in an acidic solvent and the compounds detected as shown in Table I. By serial dilutions

TABLE II

YIELDS OF ALDEHYDES (μg/g) OBTAINED BY THE METHOD DESCRIBED

	Sinapyl	*Syringic*	*Coniferyl*	*Vanillin*
Eucalyptus sp.	3000	3000	150	100
Fagus Sylvatica L. (Beech)	800	800	250	250
Tectona Grandis (Teak)	700	500	600	450
Santalum Album L.	600	500	300	200
Quercus Robur L. (Oak)	500	600	250	200
Chinese Incense	500	600	250	250
Indian Incense	100	200	100	50
Cocos Nucifera L.	300	500	300	300
Juniperus Procera Hochst	0	0	450	600
Larix Decidua (Larch)	0	0	600	600

and comparison with standard solution the content of the respective aldehydes in various woods and other materials was semi-quantitatively estimated (Table II). The values were substantially higher than in methanolic extracts of these materials.

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