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THE CATECHINS OF POLYGONUM CORIARIUM

Sh. Yu. Islambekov, A. K. Karimdzhanov, A. I. Ismailov, and A. S. Sadykov

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Continuing our study [1] of the tanning substances of the roots of P. coriarium by partition chromatography on a silica gel column, we have isolated four catechins with mp 210–211° C, 216–217° C, 170° C, and 236–237° C.

A study of the products of the alkaline cleavage of these substances showed that the first three catechins form phloroglucinol and gallic acid and the last one phloroglucinol and protocatechuic acid.

Enzymatic hydrolysis with tannase affected only the catechin with mp 210–211° C, splitting it into (–)-epigallocatechin and free gallic acid.

The IR spectra of the four catechins have broad bands at 3430–3280 cm^{-1} (closely adjacent OH groups), while the spectrum of the catechin with mp 210–211° C has additional maxima at 1710 cm^{-1} and 1140 cm^{-1} (ester linkage).

On the basis of what has been said and the results of a comparison with the catechins from tea (by paper chromatography and by mixed melting points), the compounds isolated from P. coriarium have been identified as (–)-epigallocatechin gallate, (–)-epigallocatechin, (±)-gallocatechin, and (–)-epicatechin.

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Scientific Research Institute for the Chemistry and
Technology of Cotton Cellulose, Tashkent

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TRICYCLENE IN TURPENTINES FROM PINUS SILVESTRIS

I. I. Bardyshev and E. P. Dontsova

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There is no information in the literature on the amount of tricyclene in turpentines from various species of Pinus. We have shown that tricyclene is an invariable component of all types of turpentines from the Scotch pine.

To detect tricyclene in pine oleoresin turpentine (Fig. 1, a) we distilled off the α-pinene fraction (60%, Fig. 1, b) and fractionated it in a column with an efficiency of 50 theoretical plates. The tricyclene fraction (9.3%, Fig. 1, c) was oxidized with 5% aqueous potassium permanganate at 10° C and the residue (0.04%, Fig. 1, d) was purified in a PAKhV-03 preparative gas-liquid chromatograph at 130° C in a column (5000 × 8mm) containing deactivated Inza diatomite brick (grain size 0.03–0.5 mm) impregnated with dinonyl phthalate (30% of the weight of the brick). This gave 0.003% of tricyclene $C_{10}H_{16}$ (Fig. 1, e) with mp 60° C; a mixture with an authentic sample of tricyclene melted at the same temperature.

The results of direct comparison of the IR spectra of the tricyclene that we isolated and a pure sample [1] show their complete identity (Fig. 2).

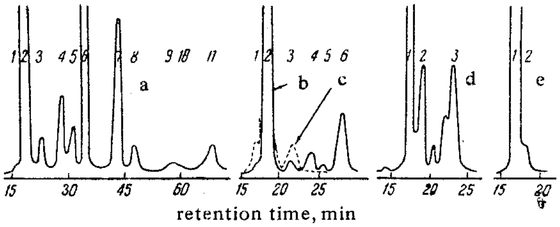
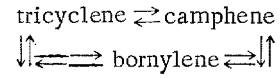


Fig. 1. Chromatograms of pine oleoresin turpentine (a); technical α-pinene (b); tricyclene fraction isolated by a fractional distillation of technical α-pinene (c); tricyclene fraction after its oxidation with $KMnO_4$ (d); and a sample of tricyclene purified on a PAKhV-03 (e). Peaks: a) tricyclene; 2) α-pinene; 3) camphene; 4) β-pinene; 5) β-myrcene; 6) 3-carene; 7) *l* + d*l*-limonene; 8) *l*-β-phellandrene; 9) p-cymene; 10) γ-terpinene; 11) terpinolene.

We have shown by analytical GLC that all types of turpentines from Pinus silvestris contain tricyclene: oleoresin turpentine 0.2%; extraction turpentine 0.3%; dry distillation turpentine 0.8%.

The analysis was carried out on a UKh-1 instrument at 115° C in a column (400 × 4 mm) containing Inza diatomite brick (grain size 0.25–0.50 mm) impregnated with tricresyl phosphate (25%).

It has not been established whether the tricyclene is present in the native turpentine or is formed during the isolation of the turpentine from the oleoresin as a result of the thermal action of acids on camphene in accordance with the scheme



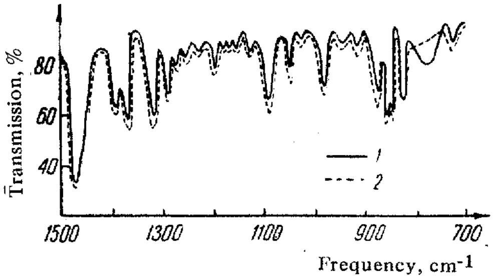


Fig. 2. IR spectra of the tricyclene isolated from turpentine (1) and a pure sample of tricyclene (2).

In the latter case, in addition to camphene [2] and tricyclene, the turpentines should also contain a small amount of bornylene.

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SESQUITERPENE LACTONES OF CYCLACHAENA XANTHIFOLIA

V. I. Novikov, Yu. N. Forostyan, and D. P. Popa

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The sesquiterpene lactone coronopilin was isolated from C. xanthifolia Fresen. (Iva xanthifolia Nutt.) (rag sumpweed) some time ago [1], and its presence in the plant was confirmed later [2].

From the combined substances obtained from a chloroform extract of the racemes (collected at the end of the flowering period in the town of Zaporozh'e), after their detection by thin-layer chromatography, we have isolated three more substances by fractional crystallization: one with mp 164–166° C (from methanol), R_f 0.14, 0.32, a second with mp 174–176° C (from chloroform), R_f 0.25, 0.75, a third with mp 126–127° C (from benzene), R_f 0.45, 0.80, and a fourth with mp 85–87° C (from benzene), R_f 0.86 [in a thin layer of alumina (activity III) in the benzene–chloroform–methanol (20 : 20 : 2) system with iodine vapor as the revealing agent] and R_f 0.90 [on silica gel G in the benzene–acetone (4 : 1) system with the spots revealed by H_2SO_4 and heating].

The substance with mp 174–176° C was identified as coronopilin by its IR spectrum and elementary composition. The substance with mp 164–166° C $[\alpha]_D^{20}$ +47.7° (c 6.5; chloroform) has the composition $C_{15}H_{20}O_4$. Its IR spectrum (KBr): 3520 cm^{-1}, 3470 (OH group), 1760 (γ-lactone), 1660, 822 (>C=CH–) cm^{-1}. There are no maxima in the UV spectrum characteristic for conjugated double bonds. The presence of the lactone ring was confirmed by saponification with aqueous alkali.

After reacidification, the initial substance was re-formed, being identified by its IR spectrum and a mixed melting point. In the usual reactions, the substance does not show the properties of aldehydes, and its IR spectrum lacks absorption bands at 2720 and 2800 cm^{-1}.

The substance with mp 126–127° C, $[\alpha]_D^{20}$ −122° (c 8.7; chloroform), had the composition $C_{17}H_{22}O_5$. IR spectrum (KBr): 3500 (OH group), 1760 (γ-lactone) 820, 860, 940, 980, 1640, 1670 cm^{-1} (double bonds); UV spectrum: λ_{max} 219, 320. The compound was not acetylated with acetic anhydride in the presence of pyridine either on heating or in the cold, which shows the tertiary nature of the OH group.

The yellow crystalline substance with mp 85–87° C, $[\alpha]_D^{20}$ −2° (c 6.5; ethanol) had the composition $C_{15}H_{18}O_3$; IR spectrum (KBr): 1760 (γ-lactone): 1640, 820 cm_{-1} (>C=CH–). No acetyl derivative was obtained by acylation under either mild or severe conditions. The substance apparently has no OH group. The IR spectrum of the noncrystalline saponification product had no band at 1760 cm^{-1}, which confirms the presence of a γ-lactone structure in the compound of the molecule.