nitrophenyl)quinoline. The reactants were stirred for 1 hr. at 10° and then for 3 hr. while the reaction mixture came to room temperature. After dissolving the tin complex in hot water, the solution was made alkaline with aqueous sodium hydroxide, extracted with benzene, and the latter evaporated. The residue was crystallized from water–acetone. The yield of pure amine was 5.3 g. (60%), m.p. 125–127°.

Anal. Calcd. for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49. Found: C, 81.69; H, 5.60.

On deamination with sodium nitrite and dilute sulfuric acid in ethanol, 7-phenylquinoline was obtained, m.p. 58–59°, and unchanged when mixed with an authentic specimen.[5]

7,8′-Biquinoline.—To a mixture of 8.8 g. of 7-(*o*-aminophenyl)quinoline, 11.4 g. of arsenic acid, and 25 ml. of 85% phosphoric acid in a three-necked flask equipped with a mechanical stirrer and reflux condenser was added 3.4 g. of freshly distilled acrolein at a temperature of 100°. After heating for 1 hr. at this temperature, the contents of the flask were poured on ice and neutralized with aqueous sodium hydroxide. The resulting precipitate was dried and extracted with 200 ml. of boiling benzene. The residue from the evaporation of the benzene was then extracted with 100 ml. of petroleum ether (b.p. 90–100°). After concentration to 50 ml., the solution was allowed to stand for several days at room temperature, whereupon crystals were deposited. Recrystallization from the same solvent yielded 0.05 g. (0.5%) of biquinoline, m.p. 193–194°. A mixed melting point with the high-melting biquinoline prepared from 2,3′-diaminobiphenyl showed no depression.

3,3′-Dinitrobenzidine—The following modification of the original procedure[6] was used: Bis *p*-toluenesulfonylbenzidine[7] (30 g.) was added slowly to 150 ml. of concentrated nitric acid keeping the temperature between 40 and 50°. The mixture was then poured on ice and filtered. After washing with water the precipitate was crystallized from aqueous dimethyl formamide; yield, 27 g. (76.1%) of product melting at 215°. (The pure product melts at 220°.) The above material was hydrolyzed by dissolving it in 250 ml. of concentrated sulfuric acid, heating it for 2 hr. on the steam bath, and pouring into ice–water; yield, 14 g. of product, m.p. 270° (lit.,[6] b.p. 275°).

3,3′-Dinitrobiphenyl.—To a mixture of 20 g. of 3,3′-dinitrobenzidine, 400 ml. of ethanol and 100 ml. of dilute (1–1) sulfuric acid there was added slowly with shaking 40 g. of solid sodium nitrite. The contents of the flask were then refluxed for 1 hr. on a steam bath, and poured on ice. The resulting precipitate was removed by filtration, dried, and extracted with benzene. After removal of the benzene the residue was crystallized from ethyl cellosolve; yield, 13 g. (73.0%), m.p. 193–194° (lit.,[8] b.p. 196–198°).

3,3′-Diaminobiphenyl.—This was prepared in the same way as 2,3′-diaminobiphenyl, and used in the following reaction without further purification.

Skraup Reaction on 3,3′-Diaminobiphenyl.—The procedure was the same as that for 2,3′-diaminobiphenyl, except that 15.3 g. of 3,3′-diaminobiphenyl was used with proportionate amounts of other reagents. On evaporation, the benzene extract solidified. Two crystallizations from benzene yielded 4.2 g. (14.7%) of a solid melting at 168–169°, and unchanged when mixed with a sample of 7,7′-biquinoline prepared by the method of Ueda.[2] Elution of the first filtrate from the above material with benzene over alumina yielded 3.5 g. of pure product (16.5%), m.p. 128–129°.

Anal. Calcd. for $C_{18}H_{12}N_2$: C, 84.35; H, 4.72. Found: C, 84.08; H, 4.69.

(5) F. H. Case and C. J. Buck, *J. Org. Chem.*, **21**, 697 (1956).
(6) F. Bell and P. Robinson, *J. Chem. Soc.*, 1127 (1927).
(7) F. Ray and L. Soffer, *J. Org. Chem.*, **15**, 1037 (1950).
(8) C. C. Barker and F. D. Casson, *J. Chem. Soc.* 4185 (1953).

Separation of Sesquiterpenes by Partition Chromatography

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The formation of pi complexes between olefins and silver salts has been the subject of numerous studies and has been utilized for isolation purposes through crystallization, countercurrent extraction, or vapor phase chromatographic techniques.

In connection with work on naturally occurring sesquiterpenes where a complementary method to vapor phase chromatography was desired, preliminary experiments with a partition chromatographic technique based upon the olefin–silver ion complex formation was investigated. Although the work had to be interrupted before the method had been thoroughly standardized, the preliminary results have proven useful in certain cases.[1-3]

Because of the lipophilic character of sesquiterpenes a reversed phase technique was employed, using glass fiber paper impregnated with hexadecane and aqueous methanol containing a high concentration of silver fluoborate as the mobile phase.[4] Silver nitrate was too insoluble to be used and concentrated aqueous silver fluoborate solutions were found to cause strong swelling of cellulose paper. Furthermore, glass fiber paper has a finer grain and offers less resistance to the mobile phase than ordinary filter paper.

After drying the developed chromatograms either by brief heating or by treatment with thionyl chloride vapor, the spots were detected by passing the paper through a solution of antimony pentachloride in chloroform. The drying process appeared to be the ambiguous part of the procedure and reproducible results were obtained only with some practice.

Using an irrigant containing approximately 90 ml. of methanol, 6 ml. of water, and 30 g. of silver fluoborate per 100 ml., the following R_f values were observed: α-Cedrene (0.15), cuparene (0.25), and thujopsene (0.46). On omitting the silver salt there was no or little separation, and the migration rates were very low. With increasing water concentration the R_f values were found to decrease. This fact was taken advantage of when dealing with polyunsaturated compounds (*cf.* ref. 2) or alcohols. Thus some cadinol mixtures were well

(1) C. Enzell, *Acta Chem. Scand.*, **15**, 1303 (1961).
(2) H. S. Barreto and C. Enzell, *ibid.*, **15**, 1313 (1961).
(3) J. Runeberg, *ibid.*, **14**, 1985 (1960).
(4) Concentrated aqueous solutions of silver fluoborate have been shown to extract volatile olefins such as ethylene out of gas mixtures. H. G. van Raay and U. Schwenk, U. S. Patent 2,913,505.

resolved by the use of a mixture of methanol (60 ml.), water (25 ml.), and silver fluoborate (50 g.) as the mobile solvent. With a slight modification the same technique has also been applied for the identification of the methyl esters of a number of resin acids.[5]

A separation on a preparative scale was carried out on a sesquiterpene mixture obtained by Runeberg[3] from the heart wood of *Juniperus thurifera* L.[6] The distilled sample gave rise to three peaks on vapor phase chromatograms,[7] two of which showed the same retention times as α-cedrene and thujopsene. Paper chromatograms showed four spots (R_f values in brackets): x (0.75), y = thujopsene (0.46), $z + u$ (0.24) and v = α-cedrene (0.15). A sample was separated on a polyvinyl chloride powder column, using hexane as the stationary phase and eluting with aqueous methanolic silver fluoborate solution. The eluate was examined by paper and vapor phase chromatography and by determination of the optical rotation.

The main fractions indicated by the optical rotation curve (Fig. 1) corresponded to the four spots on the paper chromatogram of the initial mixture. Fractions y and v gave pure thujopsene and α-cedrene,[8] respectively. Vapor phase chromatography indicated that fraction x contained two compounds, X_1 and X_2, whose combined infrared spectrum indicated the presence of *exo*-methylene groups. Compound X_2 has given dihydro-*ar*-curcumene on selenium dehydrogenation. X_1 was unseparable from α-cedrene and X_2 from thujopsene on the column used for vapor phase chromatography.

On vapor phase chromatograms fraction $z + u$ showed one large and one small peak, the latter being due to contaminating α-cedrene. The combined material from two identical runs therefore was rechromatographed in the above manner. However, on plotting the optical rotation of the eluate with the concentration of eluted material as judged by vapor phase chromatography (Fig. 2) it became obvious that besides α-cedrene at least two more compounds were present. By combining the proper fractions, compounds Z and U were obtained in a reasonably pure state. According to infrared spectra and elemental analysis, both compounds may be tricyclic sesquiterpenes containing one double bond.

The method would gain much in convenience if the silver salt solution could be employed as the stationary phase, for example by using a non-aqueous polar solvent.

(5) P. Daniels and C. Enzell, *Acta Chem. Scand.*, **16**, 1530 (1962).

(6) The separation work was carried out in collaboration with Dr. Runeberg, who subsequently carried out the chemical identification of the components isolated. The same symbols are used here as in ref. 3.

(7) J. Runeberg, *Acta Chem. Scand.*, **14**, 1288 (1960).

(8) It has been pointed out that this is probably the first time that pure α-cedrene has been isolated from a naturally occurring mixture. J. Runeberg, *Svensk Kem. Tidskr.*, **73**, 465 (1961).

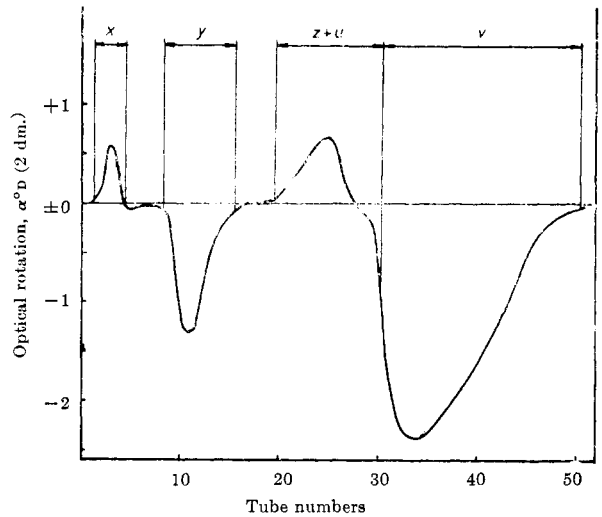

Fig. 1.—Preparative separation of sesquiterpenes from *Juniperus thurifera* L. Optical rotation of the eluate.

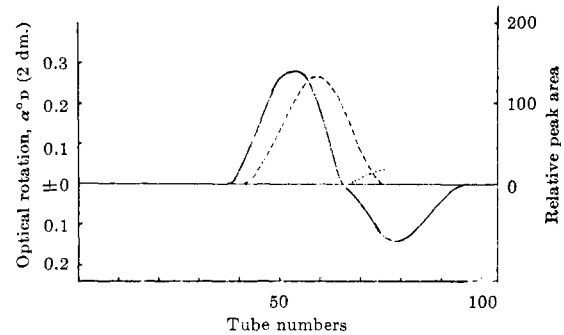

Fig. 2.—Rechromatography of fraction $z + u$. Optical rotation (——) of the eluate. Relative peak areas corresponding to compound Z or U (- - - -) and to α-cedrene (· · · · · ·) on vapor phase chromatograms.

Experimental

Silver Fluoborate Solution.—Silver oxide (755 g.) was dissolved in 1120 ml. of aqueous fluoboric acid of sp. gr. 1.23. The resulting solution, of pH 4.5, was filtered through glass paper after standing overnight and concentrated *in vacuo* to a final volume of 520 ml. (1450 g.). The product was shown to contain 12.5 equivalents of silver per liter with an estimated water content of 45% by volume. After dilution with 10 volumes of water a sample had pH 4.1. In view of the danger of acid-catalyzed rearrangements of the samples to be chromatographed it was desirable to keep the pH as high as possible without causing too extensive hydrolysis of the fluoborate, as this would limit the solubility of the product in methanol.

The chromatographic irrigant was made by mixing 9.0 ml. of methanol with 1.35 ml. of the above stock solution, giving 10.0 ml. of a solution containing approximately 30 g. of silver fluoborate and 6 g. of water per 100 ml. It was freshly prepared before use.

Paper Chromatographic Procedure.—Glass fiber paper (Schleicher and Schüll, 0.17–0.23 mm.) was cut into strips 24 cm. long with the starting line gently marked 5 cm. from the upper end. The strips were passed through a 10% solution of *n*-hexadecane in hexane, blotted between filter paper and dried. Solutions (*ca.* 4%) of the samples in pentane were spotted at 1.5-cm. intervals along the starting line but with no spot closer than 2 cm. from the edges of the paper. The chromatograms were developed in the descending way while protected from light and in an atmosphere

equilibrated with the silver fluoborate irrigant. After the solvent front had reached close to the lower end of the papers, these were dried by hanging them for about a minute in an atmosphere saturated with thionyl chloride vapors, followed by brief heating on a hot plate at about 80°. After repeated treatment with thionyl chloride and drying, the papers were passed rapidly and at an even rate through a 5–10% solution of antimony pentachloride in chloroform. After marking the spots, the papers were heated as before as this tended to intensify the color. Excessive heating had to be avoided since this gave a dark background.

The detection of the spots was quite critical and depended much upon the experience of the operator. Attempts were made simply to dry the papers at an elevated temperature prior to the antimony pentachloride treatment, but this often gave unsatisfactory results, probably because of the volatility of the samples. All operations were carried out in subdued daylight. The finished chromatograms darkened if exposed to strong daylight but otherwise they remained almost unchanged over a long period of time.

Column Chromatography.—Polyvinyl chloride powder (Wackerchemie, Germany, 72 g.) was shaken with hexane (25 ml.) in 80% aqueous methanol (400 ml.) saturated with hexane. The slurry was freed from trapped air bubbles by brief stirring under slightly reduced pressure and then added in portions to a chromatographic tube. After each addition part of the solvent was drained off while a slight positive air pressure was applied to the top of the column. The settled solid then was packed rather firmly with a plunger. The finished column (32 × 280 mm.) was washed with 90% aqueous methanol saturated with hexane, which then was replaced by the same irrigant as used for paper chromatography, but saturated with hexane.

A sample (3.00 g.) of a sesquiterpene mixture from *Juniperus thurifera*, b.p. 136–137°/25 mm., was extracted with ten 10-ml. portions of the irrigant, each being added to the column. Elution was continued with the same solvent at a rate of about 1.5 ml./min., the eluate being collected in 16-ml. portions. These were filtered through glass paper prior to determination of the optical rotation in a 2-dm. tube. The proper solutions were combined, diluted with water, and extracted with hexane. The hexane extracts were concentrated to give fraction x (0.28 g.), fraction y (0.31 g., thujopsene), fraction $z + u$ (0.80 g.), and fraction v (1.47 g., α-cedrene), indicating a total recovery of about 95%.

Since fraction $z + u$ contained some α-cedrene, material (1.65 g.) from two identical runs was rechromatographed in a similar manner, but with more of the stationary hexane phase (48 ml.) on the same amount of polyvinyl chloride powder (72 g.). The eluate was collected in 18-ml. portions. After determination of the optical rotation as before, aliquots from some of the tubes were diluted with water and extracted with hexane and the extracts were examined by vapor phase chromatography (Fig. 2). The usual work-up of the contents of tubes 39–47 afforded crude compound Z (73 mg.). The combined yield of compound U from tubes 64–69 was 298 mg. In addition there was recovered a mixture of compounds Z and U (950 mg.) and a mixture of compound U and α-cedrene (67 mg.).

Vapor Phase Chromatography.—A Pye argon chromatograph, cat. no. 12000, was used together with a Philips automatic compensator PR 2210 A/21. The column tube (length 1.20 m., i.d. 5 mm.) was packed with 100–115-mesh Silocel C 22 brick powder impregnated with 2,4-dinitrophenyl-2-naphthyl ether (15%) and dibenzylpyridine (a mixture of 2,4- and 2,6-isomers, 0.75%).[9] The column was charged with 0.025-μl. samples and was operated at 150°.

(9) A. B. Groth, *Svensk Papperstid.*, **61**, 315 (1958).

The Thermal Decomposition of Thiolsulfonates. III. Phenyl and Carboethoxymethyl Esters of α-Toluenethiolsulfonic Acid

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Previous studies[1,2] have shown that at elevated temperatures in inert solvents various diphenylmethanethiolsulfonates undergo decomposition, principally according to equation 1. The rate of the reaction is notably faster in polar solvents

$$(C_6H_5)_2CHSO_2SR \longrightarrow (C_6H_5)_2CHSR + SO_2 \quad (1)$$

(nitrobenzene, benzonitrile) than in nonpolar solvents (bromobenzene, methyl benzoate) and is also strongly dependent on the nature of R— in a manner directly proportional to the effect of R— on the acidity of the corresponding mercaptan, RSH.[3] The results clearly indicate that the sulfide sulfur atom apparently has considerable anionic character in the transition state of reaction 1.

In addition, it was found[2] that benzyl α-toluenethiolsulfonate, $C_6H_5CH_2SO_2SCH_2C_6H_5$, undergoes a similar decomposition, whose rate is also faster in polar than nonpolar solvents, but whose rate in a given solvent is about 170 times less than that of the corresponding diphenylmethanethiolsulfonate. Since this rate difference is considerably less than the 10^4–10^5-fold differences normally observed between benzyl and benzhydryl derivatives in solvolysis reactions,[5] it was considered indicative that the aralkyl fragment has considerably less carbonium ion character in the transition state of the thiolsulfonate decomposition than is the case in such typical carbonium ion reactions as solvolysis.

However, because the previous results do not rule out the possibility that the α-toluenethiolsulfonate undergoes decomposition by a different mechanism than the diphenylmethanethiolsulfonates, one can argue that this last conclusion is somewhat tenuous. To put it on a firm foundation one needs to demonstrate that the dependence on R of the decomposition rates of a series of α-toluenethiolsulfonates, $C_6H_5CH_2SO_2SR$, parallels

(1) J. L. Kice and F. M. Parham, *J. Am. Chem. Soc.*, **82**, 6168 (1960).

(2) J. L. Kice, F. M. Parham, and R. M. Simons, *ibid.*, **82**, 834 (1960).

(3) Since the submission of the previous paper accurate values for the pK_a's of the various mercaptans RSH have become available.[4] It is significant that a plot for log k_1 for the decomposition rates of the thiolsulfonates in nitrobenzene at 142° *vs.* the pK_a's of RSH shows excellent linearity and has a slope of about 0.6.

(4) M. M. Kreevoy, E. T. Harper, R. E. Duvall, H. S. Wilgus, and L. T. Ditsch, *J. Am. Chem. Soc.*, **82**, 4899 (1960).

(5) (a) A. Streitwieser, *Chem. Rev.*, **56**, 571 (1956); (b) S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Am. Chem. Soc.*, **79**, 4146 (1957).