

321. *The Selective Absorption of Optical Antipodes by Proteins.* *Part III.**

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Wool which had previously combined with sulphuric acid or 1-*p*-sulpho-phenylazo-2-naphthol combines with, and resolves, a reduced amount of mandelic or *p*-heptyloxymandelic acid. The results indicate that the anions of sulphuric acid and the arylazo-sulphonic acid also become attached to ammonium centres in wool, and that the numbers of sites on which the resolution of mandelate anions can occur is limited. A similar conclusion was reached from a study of *m*-nitromandelic acid and 5-(2 : 4-dinitroanilino)-2-*p*-toluidinobenzenesulphonic acid.

In previous communications ¹ it was shown that mandelic acid and many of its derivatives and analogues are resolved on wool by selective absorption of one of the optical antipodes from aqueous or aqueous-alcoholic solutions. The question arises whether the number of sites on which selective absorption of one of these antipodes can occur is constant. The present investigation indicates that the number is fixed, and this leads to the possibility of investigating the number of sites occupied by other, non-resolvable acids. The method of experiment adopted was to determine the amount and rotation of mandelic acid absorbed by wool under standard conditions, then to determine the extent to which the absorption and resolution were affected by the previous absorption of other non-resolvable acids. When the wool was allowed to react first with dilute aqueous sulphuric acid the amount of mandelic acid taken up was reduced, but the degree of resolution of the combined acid was not significantly altered. The result accords with the view that when sulphuric acid combines with wool the sulphate anions become attached to the same basic centres as mandelate ions would occupy in the absence of sulphuric acid. The hypothesis that sulphate ions become bound to specific sites in wool is supported by two previous investigations.² Removal of the sulphuric acid by repeated contact with water or aqueous ammonia restored the original capacity of the fibre to combine with and resolve mandelic acid. Evidently wool contains a limited number of basic sites which are capable of binding and resolving the anions of mandelic acid.

In a further experiment wool was first caused to take up 1-*p*-sulphophenylazo-2-naphthol

* Part II, *J.*, 1953, 1519.

¹ Bradley and Easty, *J.*, (a) 1951, 499; (b) 1953, 1519; Bradley, Brindley, and Easty, *Discuss. Faraday Soc.*, 1954, **16**, 152; Bradley and Brindley, *Nature*, 1954, **173**, 312; *Chem. and Ind.*, 1954, 579.

² Olofsson, *J. Soc. Dyers and Colourists*, 1952, **68**, 506; Underwood and White, *Discuss. Faraday Soc.*, 1954, **16**, 66.

from aqueous solution and then immersed in aqueous mandelic acid. The amount of mandelic acid combined and the degree of resolution were reduced by the absorbed azo-compound, the effect increasing with the amount of azo-compound present. The result favours the view that the anions of 1-*p*-sulphophenylazo-2-naphthol also are bound at the sites which would be occupied by mandelate ions in the absence of the azo-compound. As more sites are occupied by anions of the azo-compound more of the mandelic acid is bound non-selectively, possibly by hydrogen bonding at amide groups.³ Wool which is saturated with 1-*p*-sulphophenylazo-2-naphthol (0.8 mole per kg. of wool) combines with, but does not resolve, mandelic acid.

Bradley, Brindley, and Easty¹ have shown that *p*-heptyloxymandelic acid also combines with and is resolved by wool. We now find that when wool is previously combined with 1-*p*-sulphophenylazo-2-naphthol the uptake and degree of resolution of *p*-heptyloxymandelic acid are both reduced; also that little or none of the combined azo-compound was replaced on the fibre by *p*-heptyloxymandelic acid, even after five weeks at the room temperature.

m-Nitromandelic acid also combines with and is resolved by wool. Wool which had previously combined with 5-(2:4-dinitroanilino)-2-*p*-toluidinobenzenesulphonic acid combined with a reduced amount of *m*-nitromandelic acid, and the rotation of the absorbed *m*-nitromandelic acid was too small to be recorded.

EXPERIMENTAL

p-Ethoxymandelic Acid.—Ethyl *p*-hydroxymandelate (19 g.) and ethyl iodide (32 g.) were refluxed in dry acetone (200 c.c.), freshly ignited potassium carbonate (40 g.) being added during 1 hr. After 3 hr. the suspension was cooled and filtered, the solid was washed with acetone, and the combined filtrates were evaporated. The residue (18 g.) was heated for 1 hr. under reflux with 4% aqueous sodium hydroxide (250 c.c.). The resulting solution was cooled, then acidified, and extracted with ether. The dried (CaCl₂) extracts gave almost pure *p*-ethoxymandelic acid. Crystallisation from benzene afforded 13 g. of acid, m. p. 129–130°, raised to 131° after further recrystallisation from benzene (Found: C, 61.6; H, 6.0. C₁₀H₁₂O₄ requires C, 61.2; H, 6.1).

p-Pentylloxymandelic acid, m. p. 117–118° (from benzene) (Found: C, 65.5; H, 7.5. C₁₃H₁₈O₄ requires, C, 65.5; H, 7.6%), and *p*-heptyloxymandelic acid, m. p. 98° (from benzene) (Found: C, 67.6; H, 7.7. C₁₅H₂₂O₄ requires C, 67.7; H, 8.3%), were similarly prepared.

p-Decylloxymandelic Acid.—(a) Sodium *p*-decylloxymandelate (4 g.) resulted by the refluxing of ethyl *p*-hydroxymandelate (10 g.), decyl iodide (13.4 g.), and potassium carbonate (10 g.) in acetone (100 c.c.) and subsequent treatment with a solution of sodium in aqueous alcohol. The free acid (3.2 g.) had m. p. 105–106° (Found: C, 70.1; H, 9.1. C₁₈H₂₈O₄ requires C, 70.1; H, 9.1%), from benzene. (b) *p*-Hydroxybenzaldehyde (6.1 g.), decyl iodide (13.4 g.), and potassium carbonate (10 g.) were refluxed for 5 hr. The suspension was filtered, then evaporated, and the residue was dissolved in ether. The solution was cooled in ice-salt, liquid hydrogen cyanide (6 c.c.) was added, and after 12 hr. the product was isolated by evaporation under reduced pressure. Dry alcohol (4 c.c.) was added and the minimum volume of dry ether to give a solution, which was then saturated with dry hydrogen chloride at 0–5°. A deep red colour developed and crystals separated. These were collected, washed with ether, then dissolved in water (500 c.c.). Ethyl *p*-decylloxymandelate (7.5 g.) separated from the solution. The ethyl ester was refluxed for 2 hr. with a solution of sodium (2.6 g.) in alcohol (50 c.c.) containing water (2 c.c.). Crystals of sodium *p*-decylloxymandelate separated (6 g.). Acidification gave *p*-decylloxymandelic acid (5 g.), m. p. 105–106°, from benzene, identical with the product described in (a).

p-Dodecylloxymandelic acid separated from benzene as crystals, m. p. 108° (Found: C, 72.0; H, 9.4. C₂₀H₃₂O₄ requires C, 71.4; H, 9.5%).

p-Hexadecylloxymandelic acid had m. p. 111° (Found: C, 73.9; H, 10.0. C₂₄H₄₀O₄ requires C, 73.5; H, 10.2%).

2-Oxalodibenzopyran (Ring Index No. 1719).—Finely powdered aluminium chloride (32 g.) was stirred with dibenzopyran (33.4 g.) and ethoxalyl chloride (27.4 g.) in dry carbon disulphide (300 c.c.).⁴ The mixture became red, then black and viscous. When hydrogen chloride was no

³ Cf. T. Vickerstaff, "The Physical Chemistry of Dyeing," Oliver and Boyd, London, 1950, p. 301.

⁴ Cf. Adickes, Brunnert, and Luckner, *J. prakt. Chem.*, 1931, **130**, 168.

longer liberated the mixture was refluxed for 2 hr. and then evaporated. The residue was added to ice and hydrochloric acid, and the yellow product was taken up in ether and recovered by evaporating the extract. It was then heated for 2 hr. with sodium hydroxide (20 g.) in water (200 c.c.) and alcohol (300 c.c.), most of the alcohol being evaporated in the process. On being cooled the residue gave golden-yellow crystals; these were collected and washed twice with ice-water, once with acetone, and thrice with ether (yield, 25 g.). Some of the purified sodium salt was dissolved in water, the solution was acidified, and the precipitated 2-oxalodibenzofuran was extracted with ether, recovered, and finally recrystallised thrice from benzene. It formed yellow granules, m. p. 146° (Found: C, 69.9; H, 3.2. $C_{14}H_8O_4$ requires C, 70.0; H, 3.3%). The 2 : 4-dinitrophenylhydrazone, m. p. 228° (Found: N, 12.7. $C_{20}H_{12}O_7N_4$ requires N, 13.3%), formed brick-red crystals from alcohol.

Dibenzofuran-2-carboxylic Acid.—The above acid (1 g.) was dissolved in warm dilute sodium carbonate and 4% aqueous potassium permanganate was stirred in until excess was present. The solution was decolorized with sulphur dioxide, and the precipitated acid (0.7 g.) was collected, washed, and crystallised from chlorobenzene to give colourless prisms, m. p. 255° (softening at 235°) (Found: C, 73.5; H, 3.3. Calc. for $C_{13}H_8O_3$: C, 73.6; H, 3.8%). Mayer and Krieger⁵ record m. p. 246—247° with softening at 237°.

2-Dibenzofuranylglycollic Acid.—A solution of the sodium salt (10 g.) of the above glyoxylic acid in water (750 c.c.) was heated with sodium amalgam until decolorized. Acidification of the decanted solution gave colourless crystals, and these were taken up in ether and recovered (8 g.) by evaporation. Crystallisation from benzene gave the glycollic acid as prisms, m. p. 153—156° (Found: C, 69.4; H, 4.0. $C_{14}H_{10}O_4$ requires C, 69.4; H, 4.1%), which showed no reaction with 2 : 4-dinitrophenylhydrazine.

2-Naphthylglycollic Acid.—Ethyl 2-naphthylglyoxylate⁶ was refluxed for 2 hr. with 5% aqueous-alcoholic sodium hydroxide (200 c.c.). On being cooled the resulting solution afforded golden-brown crystals. These were redissolved and heated with sodium amalgam until the solution was decolorized. Acidification of the cooled filtrate then gave 2-naphthylglycollic acid (14 g.). It was extracted with ether, recovered by evaporating, and crystallised (m. p. 155—156°) from toluene (Madelung and Oberwegner⁷ record m. p. 157° for the same acid prepared from 2-naphthylglyoxal). The keto-acid gave a 2 : 4-dinitrophenylhydrazone, m. p. 237° (Found: N, 14.0. $C_{18}H_{12}O_6N_4$ requires N, 14.7%). The hydroxy-acid did not form a derivative with 2 : 4-dinitrophenylhydrazine.

9-Oxalanthracene.—Powdered anhydrous aluminium chloride (50 g.) was stirred at 0° for 0.5 hr. with a solution of anthracene (27 g.) in dry nitrobenzene (1500 c.c.). A solution of ethoxalyl chloride (21 g.) in nitrobenzene (20 c.c.) was added and the stirring was continued for 4 hr. The product was kept for 12 hr., then mixed with hydrochloric acid and ice. The solvent was distilled in steam, and the residual black tar (A) was refluxed for 3 hr. with aqueous 10% sodium hydroxide (750 c.c.). The hot solution on filtration and cooling gave golden-yellow plates (33 g.) of sodium salt. Acidification of a solution of the salt (1 g.) gave a dark orange precipitate (0.85 g.) of the acid, m. p. 186° (decomp.), which crystallised from toluene in granules of the same m. p. (Found: C, 77.3; H, 4.1. $C_{16}H_{10}O_3$ requires C, 76.8; H, 4.0%). The 2 : 4-dinitrophenylhydrazone had m. p. 240° from alcohol.

Oxidation. An aqueous solution of the sodium salt was warmed with excess of potassium permanganate. The resulting suspension was decolorised by sulphur dioxide and the precipitate of slender, yellow needles was collected. The m. p. was 284°, alone or when mixed with anthraquinone.

Ethyl ester. In a repetition of the above preparation with 9 g. of anthracene the product (A) was extracted with ether, and the soluble portion was recovered by evaporating the solvent. It was a dark, orange product which crystallized. Recrystallisation from light petroleum (b. p. 60—80°) gave large, rectangular orange plates of 9-ethoxalylanthracene, m. p. 90° (5 g.). The same compound resulted when the glyoxylic acid (16 g.) was refluxed for 12 hr. with alcohol (100 c.c.) containing 2% of hydrogen chloride. On being cooled the solution afforded golden-yellow plates (12 g.), m. p. 85—90°, which gave pure ester, m. p. 90°, from light petroleum (Found: C, 77.7; H, 4.9. $C_{18}H_{14}O_3$ requires C, 77.8; H, 5.0%).

9-Anthrylglycollic Acid.—The preceding ester (12 g.; m. p. 85—90°) was heated on a steam-bath for 24 hr. with aluminium isopropoxide (10 g.) in dry isopropanol (100 c.c.). The solvent was then evaporated, the residue was mixed with dilute hydrochloric acid, and the product

⁵ Mayer and Krieger, *Ber.*, 1922, **55**, 1661.

⁶ Blicke and Feldkamp, *J. Amer. Chem. Soc.*, 1944, **66**, 1087.

⁷ Madeburg and Oberwegner, *Ber.*, 1932, **64**, 931.

was extracted with ether. Evaporation of the extract afforded a golden-yellow resin, and this was heated for 2 hr. with aqueous-alcoholic 5% sodium hydroxide (200 c.c.), the alcohol being allowed to evaporate. The residual solution was filtered, then cooled and acidified. The yellow, crystalline precipitate was extracted with ether, recovered (10 g., m. p. 95—100°), and recrystallised from toluene as *hemihydrate*, m. p. 104—106° (Found: C, 73.0; H, 5.3. $C_{16}H_{12}O_3 \cdot 0.5H_2O$ requires C, 73.6; H, 5.0%). Further crystallisation from ethyl acetate—light petroleum gave the *acid* as pale yellow plates, m. p. 116°, of *monohydrate* (Found: C, 70.7; H, 5.2. $C_{16}H_{12}O_3 \cdot H_2O$ requires C, 71.1; H, 5.2%) which showed no reaction with 2 : 4-dinitrophenylhydrazine.

9 : 10-*Dihydro-9-anthrylglycollic Acid*.—Sodium amalgam was stirred with a hot aqueous solution of sodium 9-anthrylglyoxylate (30 g.) until the liquid had become almost colourless. It was filtered, cooled, and acidified and the precipitated *acid* was extracted with ether. Evaporation gave 24 g. of pale orange crystals, m. p. 204—205°. Recrystallisation from toluene (charcoal) gave pale orange needles, m. p. 204—205° (Found: C, 75.4; H, 5.7. $C_{16}H_{14}O_3$ requires C, 75.6; H, 5.5%).

3-*Oxalopyrene*.—Powdered anhydrous aluminium chloride (30 g.) was stirred with a solution of pyrene (18.5 g.) in dry carbon disulphide (150 c.c.). Ethoxalyl chloride (13 g.) was added and stirring was continued for 1 hr. The resulting suspension was heated for 3 hr. under reflux, then kept for 12 hr. at room temperature, and finally mixed with ice. The carbon disulphide was distilled off, and the oily suspension was heated with aqueous-alcoholic sodium hydroxide. Filtration and cooling gave yellow crystals of sodium 3-pyrenylglyoxylate (14 g.). The orientation of this acid is regarded as 3- in view of the work of Vollmann *et al.*⁸ Dissolution in water and acidification gave a precipitate of *acid* which separated from toluene as yellow granules, m. p. 138° (Found: C, 78.7; H, 3.9. $C_{16}H_{10}O_3$ requires C, 78.8; H, 3.7%). The 2 : 4-*dinitrophenylhydrazone* (Found: N, 12.6. $C_{24}H_{14}O_6N_4$ requires N, 12.3%) formed red-brown crystals, m. p. 231°, from alcohol.

By the Fischer-Speier method the acid gave its *ethyl ester* as prisms, m. p. 81° (from light petroleum (b. p. 100—120°) (Found: C, 78.5; H, 4.6. $C_{20}H_{14}O_3$ requires 79.5; H, 4.6%).

3-*Pyrenylglycollic Acid*.—This glyoxylate (8 g.) in dry *isopropanol* (100 c.c.) was refluxed for 24 hr. on a steam-bath with excess of aluminium *isopropoxide*. Evaporation gave a solid and this was extracted with ether after the addition of hydrochloric acid. Evaporation of the ether afforded a viscous, light-brown residue, and this was heated with aqueous-alcoholic sodium hydroxide, filtered, and acidified whilst hot. The 3-*pyrenylglycollic acid* which separated was extracted with ether, recovered by evaporation, and purified from *o*-dichlorobenzene. It formed light yellow crystals, m. p. 174° (decomp.) (Found: C, 78.0; H, 4.3. $C_{18}H_{12}O_3$ requires C, 78.3; H, 4.4%). A mixture of the acid with 3-pyrenylglyoxylic acid melted at 150—155°. It gave no reaction with 2 : 4-dinitrophenylhydrazine.

Absorption Experiments.—The wool employed in these experiments was Australian 64's Merino wool in the form of slubbing. It was cleaned as described by Bradley and Easty,¹⁴ and the method of experiment used by these authors was followed.

The weight of wool used was 25 g. in each experiment.

Table 1 shows the effect of previous treatment of wool with sulphuric acid on the subsequent absorption of mandelic acid. In the four experiments headed *B* wool was immersed in aqueous sulphuric acid, then in water, and finally in aqueous mandelic acid. Under *A* are two experiments in which the treatment with sulphuric acid was omitted. In each experiment a solution of 7.60 g. of mandelic acid in 500 c.c. of water was used and the duration of contact with wool was 40—45 hr., sufficient for equilibration. In experiments *B* (*a*), (*c*), and (*d*) the amount of sulphuric acid was 1.25 c.c. in 500 c.c. of water; in *B* (*b*) it was 25 c.c. in 500 c.c.

In *B* (*a*) the wool was heated for 2 hr. at 70° with the acid, then cooled, and finally rinsed in water (6 × 250 c.c.); in *B* (*c*) and (*d*) the final washing was with dilute ammonia until all [*B* (*d*)], or almost all [*B* (*c*)], sulphate ions were removed. In *B* (*b*) the same procedure was followed except that the heating was for 4.5 hr.

Table 2 shows the effect of (i) previously absorbed 5-(2 : 4-dinitroanilino)-2-*p*-toluidinobenzenesulphonic acid on the absorption of *m*-nitromandelic acid by wool, and (ii) the effect of previously absorbed 1-*p*-sulphophenylazo-2-naphthol on the absorption of *p*-heptyloxymandelic acid. In experiment 2 (*a*) the amount of the sulphonic acid previously absorbed by the wool was 7.5 g.; in 2 (*b*) it was 5.0 g. The treated wool was added in each experiment to a solution of the stated amount of *m*-nitromandelic acid in 500 c.c. of water; no measurable amount of

⁸ Vollmann, Becker, Correll, and Streeck, *Annalen*, 1937, 531, 1.

the sulphonic acid was displaced. The *m*-nitromandelic acid absorbed was recovered by means of dilute aqueous ammonia in 2 (a) and by immersion in water (6 × 500 c.c.) in 2 (b). Experiments 1 (a) and (b) show the amounts of *m*-nitromandelic acid which are absorbed from identical

TABLE 1.*

| | A | | B | | | |
|-----------------------------|--------------------|--------|--------|--------|--------|--------|
| | (a) | (b) | (a) | (b) | (c) | (d) |
| Mandelic acid : absorbed | { (g.) 2.93 | 2.80 | 1.66 | 1.24 | 2.44 | 2.74 |
| | { (mole) ... 0.019 | 0.018 | 0.011 | 0.008 | 0.016 | 0.018 |
| Mandelic acid : unabsorbed | { (g.) 4.55 | 4.60 | 5.72 | 5.85 | 5.06 | 4.73 |
| | { (mole) ... 0.03 | 0.03 | 0.038 | 0.038 | 0.033 | 0.031 |
| Mandelic acid : recovered | { (g.) 7.48 | 7.40 | 7.38 | 7.09 | 7.50 | 7.47 |
| | { (mole) ... 0.049 | 0.048 | 0.049 | 0.046 | 0.049 | 0.049 |
| Rotation of absorbed acid | +0.29° | +0.29° | +0.17° | +0.10° | +0.25° | +0.28° |
| Rotation of unabsorbed acid | -0.26° | -0.29° | -0.20° | -0.21° | -0.24° | -0.28° |
| pH of filtrate | 2.12 | 2.43 | 2.04 | 2.06 | 2.18 | 2.28 |

* For explanation of headings see text.

TABLE 2.

| | (I) 5-(2 : 4-Dinitro-anilino)-2- <i>p</i> -toluidinobenzenesulphonic | | | | (II) <i>m</i> -Nitromandelic | | <i>p</i> -Heptyloxy-mandelic | | (I) 1- <i>p</i> -Sulphophenylazo-2-naphthol | (II) <i>p</i> -Heptyloxy-mandelic |
|---|--|--------|-------|-------|------------------------------|--------|------------------------------|--------|---|-----------------------------------|
| | 1 (a) | 1 (b) | 2 (a) | 2 (b) | 3 (a) | 3 (b) | 4 (a) | 4 (b) | | |
| <i>m</i> -Nitro- or <i>p</i> -heptyloxy-mandelic acid | { (g.) ... 9.00 | 9.85 | 9.00 | 9.85 | 6.65 | 6.65 | 4.19 | 4.91 | | |
| | { (mole) ... 0.046 | 0.05 | 0.046 | 0.05 | 0.025 | 0.025 | 0.016 | 0.018 | | |
| Above acid : absorbed | { (g.) 4.82 | 5.44 | 1.54 | 1.58 | 3.93 | 3.60 | 1.99 | 1.17 | | |
| | { (mole) ... 0.025 | 0.028 | 0.008 | 0.008 | 0.015 | 0.014 | 0.007 | 0.004 | | |
| Above acid : unabsorbed | { (g.) 3.89 | 4.17 | 7.56 | 6.86 | 2.88 | 2.78 | 2.22 | 3.70 | | |
| | { (mole) ... 0.020 | 0.022 | 0.038 | 0.35 | 0.011 | 0.010 | 0.008 | 0.014 | | |
| Above acid : recovered | { (g.) 8.71 | 9.61 | 9.10 | 8.44 | 6.81 | 6.38 | 4.21 | 4.87 | | |
| | { (mole) ... 0.045 | 0.049 | 0.046 | 0.043 | 0.025 | 0.024 | 0.016 | 0.018 | | |
| Rotation of absorbed acid | +0.07° | +0.09° | — | — | +0.20° | +0.15° | +0.13° | +0.03° | | |
| Rotation of unabsorbed acid | -0.10° | -0.10° | — | — | -0.11° | -0.22° | -0.12° | +0.03° | | |
| pH of filtrate | 2.28 | 2.14 | 2.06 | 1.94 | — | — | — | — | | |

TABLE 3.

| | | | | | | | | | |
|--|--------|--------|--------|--------|--------|----------|----------|----------|-------|
| 1- <i>p</i> -Sulphophenylazo-2-naphthol on wool (mole) | 0.003 | 0.008 | 0.009 | 0.012 | 0.012 | 0.014 | 0.016 | 0.020 | 0.021 |
| Mandelic acid absorbed (mole) | 0.017 | 0.014 | 0.013 | 0.011 | 0.013 | 0.012 | 0.011 | 0.009 | 0.010 |
| Rotation | +0.27° | +0.18° | +0.20° | +0.10° | +0.16° | (+0.10°) | (+0.06°) | +0.04° | (0°) |
| Mandelic acid unabsorbed (mole) | — | 0.033 | 0.035 | 0.038 | 0.035 | 0.037 | 0.038 | 0.040 | 0.039 |
| Rotation | -0.28° | -0.24° | -0.21° | -0.14° | -0.16° | -0.12° | -0.10° | (-0.04°) | (0°) |
| pH of mandelic acid solution | 2.32 | 2.34 | 2.29 | 2.25 | 2.31 | 2.36 | 2.36 | 2.22 | 2.22 |
| Mandelic acid recovered (mole) | — | 0.047 | 0.048 | 0.049 | 0.048 | 0.049 | 0.049 | 0.049 | 0.049 |
| Acids combined with wool (mole) | 0.020 | 0.022 | 0.022 | 0.023 | 0.025 | 0.026 | 0.027 | 0.029 | 0.031 |

solutions to those used in 2 (a) and (b) when wool not previously treated with the sulphonic acid is used.

In experiment 4 (a) the amount of the sulphonic acid absorbed on the wool was 7.7 g., in 4 (b) it was 4.1 g. The *p*-heptyloxy-mandelic acid was used as a solution in 500 c.c. of aqueous alcohol containing 250 c.c. of alcohol. In 3 (a) and (b) the medium was 1 l. of aqueous alcohol containing 500 c.c. of alcohol.

Table 3 shows the amount of mandelic acid absorbed at equilibrium at the room temperature

by wool which had previously combined with the stated amounts of 1-*p*-sulphophenylazo-2-naphthol. The initial amounts of mandelic acid were 7.60 g. in 500 c.c. of aqueous solution. There was no measurable displacement of the sulphonic acid by mandelic acid.

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