ble, namely, *rac.* S_1 and *rac.* S_2. The number of possible racemates equals the number of possible tautomers.

Most racemates belong under Case 1; the designation of them as *rac.* S is quite definitive if they belong under this case. The experimental methods for the detection of such as fall under Case 1 are well known and are relatively simple. In the case of racemates which belong under Case 2, the designation *rac.* S is not definitive; obviously it must be determined experimentally whether the particular racemate is *rac.* S_1 or *rac.* S_2. The considerable number of racemic crystalline substances that have been recognized in the sugar group have always been regarded tacitly as under Case 1; it is obvious, however, as will now be shown by an example, that many of them really belong under Case 2 and that for these racemates new experimental study is required in order to classify them according to tautomeric forms. The first racemic crystals of a sugar were recognized by Ruff[1]; from a hot alcoholic solution containing equal quantities of *d*- and *l*-arabinose, well formed crystals separated on cooling; these crystals melted higher than the components and showed a much smaller solubility, which proves that they are a racemate. Ruff designated the substance "*rac.* arabinose," a name which must have appeared definitive at that time because the tautomerism of arabinose and other reducing sugars was not well recognized until later. It is now known that the mutarotation of arabinose definitely proves its tautomeric character and it is necessary to assume in the most general case that it may crystallize, under suitable conditions, as an alpha or beta form of a pyranose or of a furanose modification, or as an *aldehydo* form. There are thus five possible racemates comprised under the name "*rac.* arabinose": namely, *rac.* α-arabinopyranose, *rac.* β-arabinopyranose, *rac.* α-arabinofuranose, *rac.* β-arabinofuranose, *rac.* aldehydo-arabinose. The problem of determining which of these five racemates is represented by Ruff's "*rac.* arabinose" will require the devising of some new experimental procedure because no past observations bear upon it. Similar considerations apply to some other substances of the sugar group which have been reported as forming racemic crystals, for example some hydrazones and osazones; the mutarotation of the optically-active forms of these substances indicates tautomerism. On the other hand, the well-recognized racemate of α-methyl-mannoside[2] belongs under Case 1, since the glycosides are not tautomeric; it is definitely *rac.*-α-methyl-mannopyranoside. Likewise *rac.*-mannitol[3] and *rac.*-perseitol[4] are precise designations. An experimental study of "*rac.* arabinose" for the purpose of learning its real composition is in progress. Although the substance naturally does not exhibit "mutarotation" in the precise derivation of this term, the tautomeric change which it must undergo in solution (a sort of "masked mutarotation") should be observable through physical measurements of change of volume, refraction or solubility, or of heat of reaction, or of change of conductivity of added boric acid, to mention some of the more obvious ways. Acetylation of the racemic sugar at low temperature to yield non-tautomeric tetraacetates, which may be identifiable, seems a promising chemical method for a conclusive determination.

Drs. M. L. Wolfrom and E. F. Evans join me in expressing the opinion that the crystals of *rac.*-perseulose, which they have described recently[5] and for which they have proved the racemic nature, very probably fall under Case 2 for the reason that the *d*- and *l*-forms of perseulose exhibit mutarotation prominently.

(1) Ruff, *Ber.*, **32**, 550 (1899).

(2) E. Fischer and Beensch, *ibid.*, **29**, 2927 (1896).

(3) E. Fischer, *ibid.*, **23**, 370 (1890).

(4) W. Stanley Smith, *Ann.*, **272**, 182 (1892).

(5) Wolfrom and Brown, THIS JOURNAL, **65**, 1021 (1943).

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Model Experiments on the Use of Cyclopentadiene in the Synthesis of Sterol-like Compounds[1]

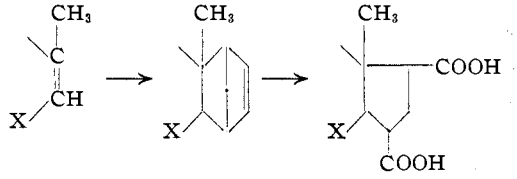
BY C. F. KOELSCH AND F. J. LUCHT

The synthesis of sterol-like compounds involves the fusion of a six-membered ring with a five-membered ring; the latter must contain a functional group, and one of the angular carbon atoms must bear a methyl group. The diene synthesis appears applicable to the formation of such substances, and attempts to use it have been made.[2] In these attempts, the six-membered ring has been formed from a diene, and the five-membered ring from a methylated cyclopentene bearing an activating group.

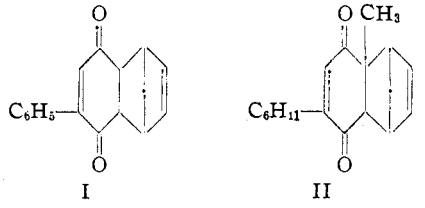
(1) This paper is from the incomplete Ph.D. Thesis of Lt. F. J. Lucht. The work is being published in its present form because military duties have necessitated postponement of the investigation by the junior author.

(2) For a discussion and references, see Woodward, THIS JOURNAL, **62**, 1478 (1940).

In the present investigation some experiments were carried out using methylated six-membered ring compounds containing activating groups; the five-membered ring was furnished by cyclopentadiene. It was intended to degrade the resulting bicycloheptene to a cyclopentane by oxidation, thus

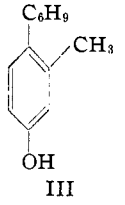


Under none of the conditions tried (seventy-two hours at room temperature, three hours at 135°, or twelve hours at 195°) did 3-methylcyclohexenone react with cyclopentadiene. But no difficulty was experienced in adding cyclopentadiene to phenylquinone or to 2-cyclohexyl-5-methylquinone. In both cases only 1:1 addition products were obtained, and it is considered that the structures indicated (I, II) are more probable than those which would result by addition to the opposite side of the quinone involved.

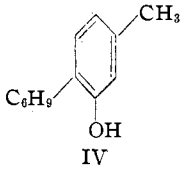


I

II



III



IV

The conjugated carbon–carbon double bond in I was reduced successfully; attempts to remove the oxygen by Clemmensen reduction gave liquid products which could not be completely purified.

The preparation of the quinone used in the synthesis of II is of interest since it establishes the structure of the product obtained by the condensation of cyclohexanone with *m*-cresol. The product was reported by Niederl and Niederl[3] to be III, but no evidence was brought forward in support of this structure. The fact that the phenol can be converted into a *p*-quinone now establishes its most probable structure as IV.

(3) Niederl and Niederl, THIS JOURNAL, **61**, 1785 (1939).

Experimental

Phenylquinone and its Addition Product (I).—Diazotized sulfanilic acid was found to be preferable to diazotized aniline in the preparation of phenylquinone, and 5-amino-2-hydroxybiphenyl was purified by crystallization of its hydrochloride from water. In other details the procedure was similar to the one described by Borsche and Scholten.[4]

A suspension of 5 g. of phenylquinone in 10 ml. of methanol and 1.8 g. of cyclopentadiene was warmed for a short time; after the quinone had dissolved, the solution was cooled and filtered. Recrystallized from methanol, the resulting **5,8-methano-2-phenyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone** (I) formed pale yellow prisms (6 g., 88%) that melted at 70.5–71°.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.6; H, 5.6. Found: C, 81.7; H, 5.7.

Reduction of **I** (6 g.) in water (120 ml.) and acetic acid (10 g. added in portions) by stirring with zinc dust at 70° for two hours gave **2,3,4a,5,8,8a-hexahydro-5,8-methano-2-phenyl-1,4-naphthoquinone,** which formed colorless stout needles (4.5 g., 75%) that melted at 149.5–152° after crystallization from methanol.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.9; H, 6.4. Found: C, 80.9; H, 6.3.

Clemmensen reduction of the hexahydro compound (10 g. in each of three experiments) gave an oily substance which contained starting material even when the reduction was continued for two days. Distillation gave a 50% yield of product, b. p. 200–215° at 23 mm., together with some higher boiling material. The product was redistilled, and the main part, which boiled at 136–138° at 4 mm., was analyzed.

Anal. Calcd. for $C_{17}H_{20}$: C, 91.0; H, 9.0. Found: C, 89.2; H, 9.3.

2-Cyclohexenyl-5-methylphenol (IV).—Prepared by the condensation of cyclohexanone with *m*-cresol according to the procedure of Niederl and Niederl,[3] this phenol (b. p. 180–190° at 25 mm.) was obtained in yields averaging 14%. An equal weight of material that boiled at 200–240° at 20 mm. was also isolated. The properties of this higher boiling material indicated that it was a dimer of cyclohexenylcresol, perhaps analogous to the one formed from 2-isopropenyl-5-methylphenol by the action of hydrochloric acid.[5]

The dimer crystallized from acetone in the form of large colorless prisms that softened at 106° and melted with effervescence at 111–113°.

Anal. Calcd. for $C_{26}H_{32}O_2 + C_3H_6O$: C, 80.0; H, 8.8; $(CH_3)_2CO$, 13.3. Found: C, 79.6; H, 8.8; $(CH_3)_2CO$, 12.1.

When the acetone-containing compound was heated to 130° and then crystallized from ethanol, the solvent-free dimer was obtained; it melted at 142–143° without effervescence.

Anal. Calcd. for $C_{26}H_{32}O_2$: C, 83.0; H, 8.6. Found: C, 83.2; H, 8.4.

2-Cyclohexyl-5-methylphenol.—2-Cyclohexenyl-5-methylphenol (10 g.) in acetic acid (40 ml.) containing platinum

(4) Borsche and Scholten, *Ber.*, **50**, 596 (1917).

(5) Fries and Fickewirth, *ibid.*, **41**, 367 (1908).

oxide (0.15 g.) rapidly took up one equivalent of hydrogen. The product boiled at 166–169° at 19 mm., and crystallized on cooling; m. p. 69–70°.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.0; H, 9.5. Found: C, 82.0; H, 9.2.

4-Amino-2-cyclohexyl-5-methylphenol.—A cold suspension of cyclohexylcresol (5.7 g.) in aqueous sodium hydroxide was mixed with a solution prepared by diazotizing 6.3 g. of sulfanilic acid. After it had stood for one hour, the mixture was treated with a solution of 14 g. of sodium hydrosulfite and then warmed until reduction was complete. The product was removed by filtration and crystallized from benzene. It formed colorless nodules (4.8 g. 78%) that became pink at 170° and melted to a brown liquid at 182°.

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.0; H, 9.3. Found: C, 76.3; H, 9.3.

2-Cyclohexyl-5-methylquinone.—A solution of the aminophenol in hot dilute sulfuric acid was poured into a solution of potassium dichromate in water. The mixture was cooled, and the product was separated by filtration (yield nearly quantitative). Crystallized from ethanol, the quinone formed bright yellow plates that melted at 60–61°.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.4; H, 7.9. Found: C, 76.3; H, 7.9.

Reduced with granulated zinc in acetic acid, the quinone yielded **2-methyl-5-cyclohexylhydroquinone,** which formed colorless plates that melted at 146–148°; yield, 95%.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.7; H, 8.8. Found: C, 75.7; H, 8.7.

2-Cyclohexyl-5,8-methano-4a-methyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (II).—A solution of 2.6 g. of 2-cyclohexyl-5-methylquinone and 2 g. of cyclopentadiene in 10 ml. of methanol was boiled for one hour and then cooled. The product was separated by filtration and recrystallized from methanol. It formed light yellow needles (3.3 g., 96%) that melted at 75–77°.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 80.0; H, 8.2. Found: C, 80.1; H, 8.2.

No trimolecular product was formed in the addition; when 1.5 g. of the product and 5 g. of cyclopentadiene were boiled for one hour in xylene, and the solvent was then distilled, there was obtained 0.9 g. of cyclohexylmethylquinone.

Reduction of the addition product with zinc and acetic acid gave a colorless product which separated from methanol in the form of nodules that melted at 71–78°. This substance has not been investigated further.

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[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY, BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

Preparation of D-Galacturonic Acid from Pectin*

BY E. RIETZ AND W. D. MACLAY

Pectin is composed principally of polymers of D-galacturonic acid and at present constitutes the most readily available source material for the preparation of this compound. Members of the medical profession are displaying considerable interest in the biological properties of not only galacturonic acid but certain of its derivatives. Due to the instability of uronic acids in hot mineral acid, enzymic hydrolysis of pectic acid has proved the most satisfactory method of preparation for galacturonic acid. Ehrlich[1] reported an enzymic method giving high yields. Mottern and Cole,[2] employing the domestically-available materials, pectic acid and "Pectinol 46 AP,"[3] obtained the uronic acid in a yield of approximately 25 per cent. Manville, Reithel and Yamada[4] modified the method of Mottern and Cole to give a maximum yield of 36%. Pigman[5] further modified this method by using methanol in place of ethanol as an extracting solvent and obtained yields in excess of 67% of the weight of the uronic anhydride content of the pectic acid employed as a source material.

The preparation of D-galacturonic acid directly from pectin instead of from pectic acid was undertaken because of the somewhat laborious intermediate preparation of the pectic acid when carried out in the laboratory and the non-uniformity of commercially-available pectic acid. A number of commercial pectins have been used and yields of D-galacturonic acid ranging from 74 to 80%, based on the uronic anhydride content of the pectin, are readily obtainable. Included in these were 285- and 300-grade apple pectins and 170-, 185- and 200-grade citrus pectins with average yields of 78, 78, 80, 78, and 74%, respectively, of the uronic acid.

Experimental

Four 100-g. lots of a 300-grade apple pectin (uronic anhydride content 76.6%) were each dispersed in 2000 ml. of water by means of a Waring Blendor and adjusted to a *p*H of 3.7 by the addition of 20 ml. of 3 *N* sodium hydroxide. The pectin solutions were transferred to 3-liter Erlenmeyer flasks, 10 g. of Pectinol 46 AP was added to each, and the surfaces were covered with toluene. The reaction mixtures were placed in a 30° room for ten days, the course of the hydrolysis being observed by hypoiodite oxidations. Normally, over 50% of the hydrolysis occurs during the first twenty-four hours, and 75 and 95% within three and

(1) F. Ehrlich, "Abderhaldens Handbuch der biologischen Arbeitsmethoden," Abt. 1, Teil II, 1617 (1936).

(2) H. H. Mottern and H. L. Cole, THIS JOURNAL, **61**, 2701 (1939).

(3) Röhm and Haas Pectinol 46 AP, standardized with diatomaceous earth.

(4) I. Manville, F. Reithel and P. Yamada, THIS JOURNAL, **61**, 2073 (1939).

(5) W. W. Pigman, *J. Research Natl. Bur. Standards*, **25**, 301 (1940).