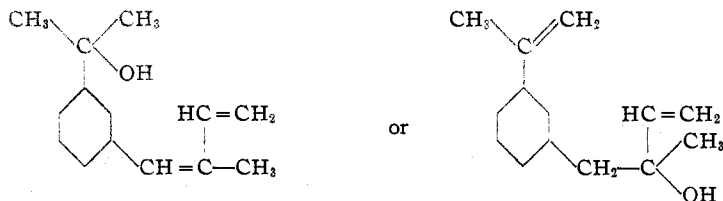


to be the case with zingiberene. If the constitution advanced by Semmler for zingiberene and *iso*-zingiberene are correct, then the constitution of zingiberol is probably one of the following:



In working with ginger oil, the author was much impressed by the rapidity with which resinification occurs. This is particularly true of the pure hydrocarbon zingiberene, which, as Semmler has shown, contains two conjugated double bonds, as in myrcene and isoprene. The author's experience with both the distillation and extraction of fresh vetiver root, the essential oil of which also consists chiefly of sesquiterpenes and their derivatives, proved that better yields of oil were obtained and that the oil was of much superior quality when the roots were distilled or extracted within a few days of their harvest than after storage several months, as must necessarily be the case with roots shipped to Europe for distillation there. It is highly probable, therefore, that distillation or extraction of the freshly harvested ginger rhizomes would give better oil and in relatively larger yields than the dried material usually employed.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, THE UPJOHN COMPANY.]

SOME CONSTITUENTS OF SUMBUL ROOT.

BY FREDERICK W. HEYL AND MERRILL C. HART.

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Since the root of *Ferula Sumbul* is an officially recognized drug of the United States Pharmacopoeia, and has for some years been used as an antispasmodic, it was deemed of interest to subject the root to a more complete chemical investigation. Our present knowledge of its constituents is fairly summarized in the United States Dispensatory¹ where it is stated that the root contains a volatile oil, two balsamic resins, wax, gum, starch, a bitter substance, fat (17%), angelic and valeric acids. Knitl,² with Tschirch, isolated umbelliferon. Cushny³ classifies sumbul with valerian, basing the similarity upon the presence of malodorous volatile oils, which may act psychically and physiologically. Since the oil of sumbul, in consequence of the study of the other constituents re-

¹ *U. S. Dispensatory*, 19th Ed., 1209.

² *Archiv. Pharm.*, 237, 270 (1899).

³ "Pharmacology and Therapeutics," 73 (1906).

ported in this paper, appears to be important in this connection, we shall report upon it later.

It is generally stated that the musk root now upon the pharmaceutical market in the United States is not true *Ferula sumbul*; but that in its place we have the dried rhizome and root of an undetermined umbelliferous plant, which enters commerce from Central and Northern Asia, through the Moscow drug market. Our sample consisted of the unsliced root imported from Moscow. Further than this it was impossible to trace its origin. The root was of a quality which is now considered official.

The proximate analysis shows that the air-dried root contained 10.2% moisture and 6.5% ash. Lignoïn extracted, 11.8%; ether, 14.6%; and alcohol, 27.4%. The residue insoluble in alcohol had the following composition: crude fiber, 17.5%; pentosans, 10.6%; protein, 5.4%; starch, 7.7%; dextrin, 1.4%. The alcoholic extract, which contains the substances entering into pharmaceutical preparations, showed the presence of 1.7% sucrose, approximately 1.0% levulose, and the resin after hot extraction amounts to 18.7%. There is a very considerable discrepancy in the extractive matter removed by alcohol, depending upon the temperature. Whereas boiling 95% alcohol extracted 27.4% of sumbul root, the cold percolation which was exhaustively completed, extracted only about 20%, and about 17.3% was precipitated by the addition of water.

The products present in the alcoholic solution (obtained by cold percolation) and soluble in water besides the sugars above mentioned, are acetic acid, a glucoside of umbelliferon, and betaine.

The resin insoluble in water, which forms the most conspicuous portion of this drug, was extracted successively with lignoïn, ether, chloroform, ethyl acetate, and alcohol.

The lignoïn extract consisted to the extent of about 17% of resinous material other than fat. This product was a white acid resin, soluble in one per cent. potassium hydroxide, and yielded upon hydrolysis vanillic acid and an oil resembling the volatile oil. The fat yielded a large amount of indefinite unsaponifiable material, of which one fraction showed a constant boiling point at 168–173° at 12 mm. and upon analysis gave values indicating the formula $C_8H_{18}O$. The unsaponifiable matter further yielded a phytosterol, $C_{27}H_{46}O$, melting at 134–135°. The corresponding acetate melts at 121–122°. The following fatty acids were identified: acetic, butyric, valerianic, tiglic, angelic, oleic, linoleic, cerotic, palmitic and stearic acids.

The ether extract of the resin, yielded a phytosterolin, $C_{33}H_{58}O_8$, melting at 290°. It formed an acetate that melted at 159–160°. A trace of vanillin was indicated by color tests. The ether extract consists of neutral resinous (42%) and acidic resinous (52%) constituents. The former proved to be an ester, and yielded umbelliferon and therefore

belongs with the group that includes galbanum, sagapen and asafoetida. The acidic resin could be prepared as an almost white powder, but fractional extraction indicated this to be a mixture of resin acids. These acids upon hydrolysis yield both vanillic acid and umbelliferon.

The chloroform extract of the resin consisted largely of a resinous glucosidic substance. It yielded umbelliferon and glucose upon hydrolysis.

The product extracted from the resin with ethyl acetate was not glucosidic but umbelliferon was prepared from it after hydrolysis.

The alcoholic extract of the resin also yielded umbelliferon and a reducing sugar upon hydrolysis.

Experimental.

A. Proximate Analysis (By Mr. J. F. Staley).—A sample of the air-dried root after grinding and sieving was quantitatively extracted with various solvents and the following results were obtained:

Extract.	Per cent.
Ligroin (35-55°).....	11.72, 11.83
Ether (110°).....	14.66, 14.55
Volatile ether extract.....	(see below, volatile oil)
Alcoholic.....	27.6, 27.14

The proximate analyses were conducted in accordance with the usual methods¹ and gave the results tabulated below:

	Per cent.	Per cent.
Moisture.....	10.17	Protein..... 5.5, 5.3
Starch (diastase).....	7.7	Ash..... 6.5, 6.4
Pentosans.....	10.6	Dextrin..... 1.4
Crude fiber.....	17.15, 17.6	

A determination of the alcohol soluble carbohydrates was carried out by completely extracting 100 g. of the root with boiling neutral alcohol. The combined alcoholic extracts were concentrated under diminished pressure to a small volume, and enough water was added to completely precipitate the resin. This mixture was shaken repeatedly with ether in the volumetric flask, in order to remove as much of the resin as possible. The ether was removed with a pipet. The last traces of ether were removed by passing a current of air through the solution, which was thereupon precipitated with an excess of basic lead acetate solution and made up to a volume of 200 cc. This solution was filtered and the filtrate showed a rotation of -1.78° V, at 20° in a 2 dcm. tube. Lead was removed from the solution and 12.5 cc. were inverted by permitting it to stand in the presence of hydrochloric acid for 24 hours. The solution was neutralized and made up to a volume of 50 cc. This showed a rotation of -0.6° in a 2 dcm. tube. The percentage of sucrose calcu-

¹ U. S. Dept. Agr., Bur. of Chem., *Bull.* 107 (revised).

lated by Clerget's formula is 1.64%. It is further indicated that the reducing sugar is levulose in an amount of approximately 0.51%. Gravimetric estimations of the sugars by the Munson and Walker modification of Fehling's process gave 1.87% sucrose and 1.0% of reducing sugar.

Sumbul root was examined for the presence of alkaloids by extracting a 200 g. sample with Prolius' solution but with negative results.

Volatile oil was determined, first by steam distilling one kilo of the coarsely ground drug for a few hours. The yield was 6.8 g. oil corresponding to 0.68%. When a 500 g. sample of finely sieved material was distilled for several days 5.51 g. of oil (1.1%) was obtained.

The oil on standing deposited a few yellow crystals that melted at 113–114° but these were not identified. The oil had a specific gravity of 0.932 at 15°. Upon distillation the higher fractions turned dark blue in color. A qualitative test for sulfur was negative.

B. Complete Examination of Alcoholic Extract.—For this purpose 56.7 kg. were exhausted by percolation with cold 95% alcohol. The percolate (327 l.) was concentrated under diminished pressure to a volume of 15.7 liters (1 l. = 3.6 kg. sumbul root).

Two liters of this extract were poured into 8 l. of distilled water and vigorously shaken. A heavy, sticky, viscous, light brown, semi-liquid separated. After standing 24 hours the aqueous layer was decanted, and the resin was washed with a second addition of distilled water. The resin weighed 1231 g. = 17.1%. A second 2 liter portion gave 1251 g. A third lot was precipitated and the resin fraction on the one hand, and the fraction representing the water-soluble constituents on the other, were studied separately.

The Examination of the Water-Soluble Constituents.—This solution (30 l.) contained the water-soluble constituents from 6 l. of the alcoholic extract representing 21.6 kg. of the root. It contained 520 g. of material and was concentrated to a volume of 3 l. under reduced pressure. The distillate obtained was distinctly acid. It was therefore rendered alkaline with barium hydroxide and concentrated to a small volume, again rendered acid and steam distilled. Acetic acid was identified as the silver salt.

Calc. for $C_2H_3O_2Ag$: Ag = 64.6. Found: 64.1%.

The concentrated solution was extracted repeatedly with large volumes of ether. The ethereal solution, which contained 46 g. of material, was concentrated to a small volume and fractionally extracted with solutions of hydrochloric acid (10%), water, ammonium carbonate, sodium carbonate, and potassium hydroxide successively. Nothing definite was isolated from these fractions, although the sodium carbonate fraction upon acidification yielded slight amounts of crystalline material.

The aqueous solution which had been completely extracted, was ex-

tracted with chloroform, which removed 13 g. of dark, oily material, from which nothing of a crystalline nature could be obtained. The aqueous layer, after the above-mentioned ether and chloroform extractions, was repeatedly shaken with hot amyl alcohol. The combined amyl alcoholic extracts were concentrated and washed repeatedly with water until free from reducing sugar. Upon further concentration of the amyl alcoholic extracts several crops of brown amorphous hygroscopic material separated. These could not be crystallized. The amyl alcohol was completely removed. Altogether 122 g. of material were present in this fraction, but its dark-colored, varnish-like nature prevented crystallization even after prolonged standing. For acid hydrolysis 42 g. were digested for two hours with 5% dilute alcoholic sulfuric acid. Upon removal of the alcohol, a smear separated. Water was added and the whole subjected to a steam distillation. The oily distillate which had an odor resembling furfuraldehyde failed to give the furfuraldehyde test. When the contents of the flask which had been steam-distilled had cooled a black resin separated, in which were admixed wart-like aggregates of crystalline material. The resin was therefore repeatedly extracted with boiling water. This was facilitated by blowing steam through the mixture. Altogether 2.9 g. of crystalline material separated from these watery extractions. The product was crystallized from dilute alcohol and from hot water. It separated in beautiful star-like aggregates of fine needles, melting at 227°. These crystals gave a blue fluorescence in alkaline solution. They were identified as umbelliferon.

Calc. for $C_9H_6O_3$: C, 66.67; H, 3.7. Found: C, 66.63; H, 3.9.

The black resin was dissolved in alcohol, poured upon purified sawdust and extracted with various solvents, but no crystalline compounds were isolated from it.

The combined acid aqueous liquid from which umbelliferon had crystallized, was concentrated to a small volume and extracted with ether, which dissolved a further quantity of umbelliferon. The sulfuric acid was quantitatively removed from the aqueous solution, from which *d*-phenyl glucosazone melting at 204–205° was prepared. No pentose sugar was present. The quantity of reducing sugar present was equivalent to 11.27 g. glucose.

One of the products extracted by amyl alcohol is therefore distinctly shown to be glucosidic in nature, and is undoubtedly a body similar or isomeric with the glucoside of *Skimmia japonica*.¹

The aqueous liquid which had been extracted with ether and with amyl alcohol was freed from the latter immiscible solvent by means of a vigorous steam distillation. The total volume at this point was 10 liters.

The distribution of nitrogen in this solution was as follows: Total

¹ Eykman, *Receuil trav. chim. pays-bas.*, 1884, p. 204.

soluble nitrogen, 3.8 g. or 0.017%; ammonia nitrogen, 1.23 g. or 0.0057%; lead subacetate precipitable nitrogen, 1.31 g. or 0.0068%; nitrogen precipitated with phosphotungstic acid, 0.463 g. or 0.0021%.

In order to test for acid amides such as asparagine and glutamine, one-fifth of the solution was precipitated with mercuric acetate solution, but only a very slight separation took place. Its subsequent examinations for asparagine, glutamine, and allantoine were negative.

The remaining four-fifths was completely precipitated with basic lead acetate, whereupon a precipitate separated. This was removed by filtration and decomposed with hydrogen sulfide in the usual manner. The material precipitated with lead subacetate weighed but six grams. The usual tests for tannin were negative. It was mixed with purified sawdust and extracted with various solvents but this led to no pure products. An alkaline hydrolysis yielded no definite compounds.

The filtrate from the lead subacetate precipitate was freed from the excess of lead with hydrogen sulfide and after filtering off the lead sulfide, the filtrate was concentrated to a syrup. A small portion of this syrup, which has been shown to contain levulose and sucrose yielded a heavy crystalline deposit of pure *d*-phenylglucosazone which melted and decomposed at 210–211°. Pentose sugars were absent.

The remainder of this solution was precipitated with an excess of phosphotungstic acid in the presence of 5% sulfuric acid, and the resulting precipitate was removed by filtration, washed with 5% phosphotungstic acid wash and decomposed by the method of Wechsler.¹

The solution of the basic products was made up to a volume of 500 cc.

25 cc. distilled with MgO yielded no ammonia.

25 cc. required by the Kjeldahl method 12.58 cc. 0.1 *N* acid.

The remainder of the solution of basic products was concentrated to a syrup at 33°. This was extracted with 150 cc. of absolute alcohol and filtered. The alcohol was removed, and upon again treating the residue with absolute alcohol an amorphous hygroscopic solid separated. The filtrate from this now proved to be freely soluble in absolute alcohol and upon the addition of concentrated hydrochloric acid crystals consisting chiefly of betaine hydrochloride separated. The yield amounted to 0.5 g. or 0.019%. These crystals were not quite homogenous. After several crystallizations from alcohol the melting point was about 229–232°. Some parts of the crystalline mass which had the typical appearance of betaine hydrochloride could be picked out, and after rinsing with absolute alcohol the melting point found was 235°. The chlorine determination also indicated the presence of another base.

Calc. for $C_6H_{11}O_2N.HCl$: Cl, 23.1%. Found: Cl, 24.5%.

¹ *Z. physiol. Chem.*, 73, 138 (1911).

Pure betaine was identified after a fractional crystallization as the gold salt.

Calc. for $C_5H_{12}O_2N.AuCl_4$: Au, 43.1%. Found: Au, 43.2%.

Cholin was absent. A fractional crystallization of the mercuric chlorides failed to indicate any separations. The most insoluble fraction of the mercuri-chlorides when decomposed with hydrogen sulfide, and converted into the corresponding gold salt yielded a very pure sample of betaine aurichloride melting at 246–247° and containing 43.1% gold. The melting point of the following fraction was 239–240° and it contained 42.7% gold. The base here is chiefly betaine, but another substance is also present in the fraction.

The Examination of the Resin.—The resin precipitated when the alcoholic extract was poured into water weighed about 3.7 kg. This in alcoholic solution was poured upon purified sawdust, after it had been ascertained that nothing crystalline could be directly separated from it. A suitable quantity of the dried impregnated sawdust was transferred to a continuous extractor and extracted with the following results:

Petroleum ether (40–60°).....	357 g.
Ether.....	316
Chloroform.....	46
Ethyl acetate.....	19
Alcohol.....	18
Total.....	756 g.

The Ligroin Extract.—This extract amounted to 357 g. It was dissolved in 2 liters of ether and then extracted with solutions of hydrochloric acid, water, and ammonium carbonate. None of these extractions yielded definite products. The ethereal solution was now shaken with a solution of potassium carbonate whereupon an emulsion formed. The mixture was acidified and then a clear ethereal solution was recovered which was successfully extracted with a ten per cent. solution of potassium hydroxide. The combined potassium hydroxide extractions were acidified and extracted with ether, and from this ethereal solution the substances soluble in aqueous potassium carbonate solution could now be extracted, leaving at length an ethereal solution containing 62 g. The constituents of the ether solution which were soluble in potassium carbonate solution were again extracted with ether after acidifying the solution of the potassium salts. The solution was dried over anhydrous sodium sulfate and the ether removed. The residue which weighed 32 g. was distilled under diminished pressure. The boiling point was 234–275° at 28 mm. and it had an iodine number of 101.3. These fatty acids were studied in connection with those obtained upon the subsequent hydrolysis of the glycerides.

The material soluble in potassium hydroxide solution was almost

entirely removed from its ether solution by fractional extraction with one per cent. potassium hydroxide solution. Upon acidification this resin could be obtained as a brittle solid. It yielded the same products when hydrolyzed in acid and in alkaline alcoholic solution. The acid hydrolysis, however, was more satisfactory, and after heating for many hours with 5% alcoholic sulfuric acid the alcohol was removed by steam distillation.

The steam distillate yielded a small quantity of an oil resembling the volatile oil of sumbul. The fraction boiling below 230° was colorless while the fraction boiling at 230–250° was dark blue in color.

The black resinous hydrolysis products, contained in the flask were extracted with ether. The ether was extracted with solutions of ammonium carbonate, potassium carbonate, and potassium hydroxide. From the ammonium carbonate extract, vanillic acid was obtained. It melted at 206.5 to 207.5°. It was dried at 125° and analyzed.

Calc. for $C_8H_8O_4$: C, 57.1; H, 4.8. Found: C, 57.1; H, 4.7.

The methyl ester, prepared in the usual manner, melted at 62–63°.

The potassium carbonate extraction showed a blue fluorescence, but nothing could be obtained from it. The potassium hydroxide solution removed most of the hydrolytic products. These were recovered and again hydrolyzed with a further quantity of 5% alcoholic sulfuric acid, but no further yield of vanillic acid was obtained. The material soluble in potassium hydroxide solution was fractionally distilled at a pressure of 17 mm. Five fractions were obtained: (I) up to 150°, (II) 150–170°, (III) 170–205°, (IV) 205–212°, (V) above 212°. Fractions I, II, III were solids from which a considerable quantity of vanillic acid (206–207°) was isolated. The upper fractions were amber-colored oils that solidified. They resemble somewhat the higher boiling fractions obtained in the unsaponifiable fraction of the fat.

The original ethereal solution which had been extracted as described above was evaporated to dryness and the residue of neutral substances was saponified by boiling with 700 cc. of ten per cent. alcoholic potash for about seven hours. The alcohol was removed and water added in sufficient quantity to completely precipitate the unsaponifiable material. This was extracted with ether.

Examination of the Unsaponifiable Matter.—The dried solution was evaporated to dryness and the residue proved to be an oil which could not be directly crystallized. The material was divided into two equal parts and fractionally distilled under diminished pressure. The results upon the first half were as follows:

Fraction I. (B. p. 100–174° at 27–24 mm.) This was a yellowish limpid oil with a somewhat fragrant odor and amounted to about 7 g.

Fraction II. (B. p. 174–190° at 25 mm.) This is an olive-green

oil amounting to about 11 g. The viscosity seemed to increase noticeably and the fraction was therefore stopped at 190°.

Fraction III. (B. p. 190–205° at 28 mm.) This was a thick olive-green oil amounting to about 14 g.

Fraction IV. (Up to 267° at 30 mm.) This is a thick viscid fraction which did not solidify and weighed about 23 g.

Fraction V. (B. p. 290–360° at 17 mm.) This weighed 4.4 g. and partially solidified.

The other half of the unsaponifiable material was distilled in approximately the same manner and the light, limpid fragrant oils which constitute the lower boiling fractions were fractionally distilled several times.

The fractions were as follows:

Fraction I. (Up to 140° at 15 mm.) This fraction had no sharp boiling point as some of the material boiled at 80°. It is a very mobile yellow oil.

0.1807 g. absorbed 0.301 g. iodine; iodine number, 166.6. 0.1902 g. subst. gave 0.1815 g. H₂O and 0.5564 g. CO₂. Found: C = 79.8; H = 10.7.

Fraction II. (B. p. 140–170° at 18 mm.) This is a yellow oil, slightly less mobile than Fraction I. It was rather fragrant and was unsaturated.

Fraction III. (B. p. 175–180° at 15 mm.) This fraction appeared to possess an almost constant boiling point. It was redistilled and most of it passed over at 168–173° at 12 mm. It was light green in color and not more than slightly mobile unless warmed. The specific gravity at 15° was 1.0052 and $[\alpha]_D^{26}$ was -17.41° .

2.3353 g. made up to 20 cc. with chloroform showed a rotation of -4.06° in a 2 dcm. tube

0.1393 g. subst. absorbed 0.2432 g. iodine; iodine number, 174.6. 0.1982 g. subst. gave 0.1482 g. H₂O and 0.5596 g. CO₂. Calc. for C₈H₁₈O: C = 76.75; H = 10.5. Found: C = 77.0; H = 10.4.

The other fractions boiling above 180° and below 270° were thick viscid oils and seemed similar to the material which usually accompanies the phytosterols in this fraction, but the amount present in sumbul root is unusually large. It amounted to about one-half of the entire fraction.

The highest boiling fraction yielded, when crystallized from ethylacetate, 2.0 g. of a phytosterol melting at 134–135°.

Calc. for C₂₇H₄₆O.H₂O: H₂O = 4.5. Found: 4.97.

Calc. for C₂₇H₄₆O: C = 83.9; H = 11.9. Found: C = 84.0; H = 12.1.

0.4786 g. anhydrous material made up to 20 cc. with chloroform showed a rotation of 1.42° in a 2 dcm. tube, whence $[\alpha]_D^{20} = -29.7^\circ$.

It yielded an acetyl derivative, that separated from acetic anhydride in thin, elongated plates terminating in an angle at one end, and melting at 121–122°. When recrystallized from ethyl acetate the melting point was unchanged. The filtrate from which this 2 g. of phytosterol separated

yielded upon concentration 1.3 g. further. Recrystallized once it melted at 133–134° and yielded an acetate identical in appearance with the one just described. The melting point of the acetate separating from acetic anhydride was 118–120° which was elevated to 120–121° by one recrystallization.

Examination of the Volatile Fatty Acids.—The alkaline solution from which the unsaponifiable matter had been extracted with ether was divided into two equal parts, each of which, after acidification with dilute sulfuric acid, was steam distilled for eight hours. The odor of the distillate resembles that of infusion of hops. The combined distillate was almost neutralized with 656 cc. of 0.41 *N*, barium hydroxide solution. This was concentrated under diminished pressure to a volume of 200 cc. and acidified with hydrochloric acid, whereupon a quantity of oil separated which was extracted with ether. The solution was dried over anhydrous sodium sulfate and the ether removed. The residue, weighing about 17 g. was fractionally distilled at atmospheric pressure. The distillate was caught in three fractions: (I) up to 157°; (II) 157–190° (6.2 g.); (III) 190–200° (9.5 g.). The third fraction, when allowed to stand in the ice chest, yielded a crop of beautiful crystals of tiglic acid melting at 61°. The fractions above recorded were now subjected to a systematic fractional distillation and five fractions were obtained.

Fraction I. (B. p. up to 125°.) This fraction was neutralized with ammonium hydroxide, concentrated in order to remove the excess of ammonia and treated with silver nitrate solution. It contained a small quantity of acetic acid as was shown by the analysis of the silver salt that separated.

0.1171 g. gave 0.0717 g. silver. Calc. for $C_2H_3O_2Ag$: Ag = 64.6%. Found: 61.2%.

Fraction II. (B. p. 125–165°.) This was an intermediate fraction, amounting to about 3 g. It had the odor of acetic acid combined with that of valerianic or butyric acid.

0.1331 g. gave 0.1050 g. H_2O and 0.2377 g. CO_2 . Found: C = 48.7; H = 8.85.

Calc. for $C_2H_4O_2$: C = 40.0; H = 6.7%; for $C_4H_8O_2$: C = 54.5; H = 9.1%; for $C_5H_{10}O_2$: C = 58.8; H = 9.8%; for $C_6H_{12}O_2$: C = 60.0; H = 8.0%.

The analytical data indicates a mixture of butyric and acetic acids.

Fraction III. (B. p. 165–180°.) This fraction had the odor of butyric and valerianic acids. When dissolved in aqueous solution of sodium carbonate it instantly reduced potassium permanganate solution in the cold and it therefore contained a quantity of unsaturated acid.

0.2152 g. gave 0.1549 g. H_2O , and 0.4308 g. CO_2 . C = 54.6; H = 8.1.

This fraction consists essentially of butyric and angelic acids.

Fraction IV. (B. p. 180–190°.) C = 59.7; H = 8.33. This fraction was converted into the silver salts which had a constant composition

Calc. for $C_4H_7O_2Ag$: Ag = 55.4; for $C_5H_9O_2Ag$: Ag = 51.7; for $C_6H_7O_2Ag$: Ag = 52.2. Found: I, Ag = 52.1; II, Ag = 52.0.

Fraction V. (B. p. 190–195°.) C = 59.8; H = 8.1.

These fractions are mixtures of angelic and tiglic acids. The solid acid which was repeatedly separated by freezing the high boiling fraction, melted at 62–63°, and when analyzed gave results agreeing with those required by tiglic acid.

Calc. for $C_5H_9O_2$: C = 60.0; H = 8.0. Found: C = 60.1, H = 8.1.

The aqueous liquid from which the above-described acids had been extracted with ether was again steam distilled and yielded a crop of crystals of almost pure silver acetate.

Calc. for $C_5H_9O_2Ag$: Ag = 64.6. Found: Ag = 64.1%.

Examination of the Nonvolatile Fatty Acids.—The acid mixture which had been steam distilled for the removal of the fatty acids was cooled and extracted with ether. From the dried solution the ether was removed and the residue digested with a large volume of low boiling petroleum ether. A considerable quantity of a sticky, brown smear proved to be insoluble. The petroleum ether was removed and the fatty acids distilled. They had an iodine number of 121, and boiled chiefly at 230–260° at 15 mm. However, a considerable quantity came over at lower temperatures, showing that the steam distillation had not completely removed the lower acids. The first distillate crystallized upon cooling and proved to be tiglic acid melting at 63–64°. Furthermore a fraction boiling above 260° was caught. The weight of these acids was 19.2 g.

This was mixed with the acids which had been originally extracted with potassium carbonate solution. Of this mixture a portion weighing 22.4 g. was separated into the solid and liquid acids. The latter weighed 16 g., thus constituting about 71% of the fatty acids. These boiled chiefly at 215–245° at 15 mm., although they seemed to contain a trace of the lower acids.

Calc. for $C_{18}H_{34}O_2$: C = 76.6; H = 12.1; iodine no. = 90.1; for $C_{18}H_{32}O_2$: C = 77.1; H = 11.4; iodine no. = 181.4; for $C_{18}H_{30}O_2$: C = 77.7; H = 10.8; iodine no. = 274.0. Found: C = 77.3; H = 11.2; iodine no. = 138.7, 138.7.

The liquid acids therefore consist of oleic and linoleic acids with perhaps a small quantity of linoleic acid.

The solid acids weighed 4.1 g. A quantity of cerotic acid equivalent to 33% of the solid acids was obtained. It melted at 74–75°.

Calc. for $C_{26}H_{52}O_2$: C = 78.8; H = 13.1; N. V. = 141.7. Found: C = 78.4; H = 13.0. N. V. = 140.7.

The alcoholic filtrate from the cerotic acid yielded a quantity of a mixture of palmitic and stearic acids melting at 52–53°.

Calc. for $C_{16}H_{32}O_2$: C = 75.0; H = 12.5; N. V. = 219.1; for $C_{17}H_{34}O_2$: C = 76.1; H = 12.7; N. V. = 197.5. Found: C = 75.6; H = 12.5; N. V. = 205.3.

The **Ether Extract of the Resin**, which amounted to 316 g., was obtained in two extractions of the sawdust which had been impregnated with the resin, as above described. The first extract amounting to 300 g. was very soluble, while the second ether extract (16 g.) was obtained by prolonged extraction and upon standing tended to separate as a tar.

The first extract was concentrated and after prolonged standing a small quantity of a white micro-crystalline product separated. When this substance was dissolved in chloroform, in the presence of a few drops of acetic anhydride, and sulfuric acid was added a play of colors resulted showing at first transient pink, then blue, and finally a beautiful green. It melted at 260–270°, and after crystallization from dilute pyridine it melted at about 290°. It was a phytosterolin.

Calc. for $C_{33}H_{56}O_6$: C = 72.3; H = 10.2. Found: C = 72.6; H = 10.2.

A small portion was converted into an acetate, which crystallized from a mixture of dilute alcohol and ethyl acetate in beautiful plates, melted at 159–160°.

A portion of the ethereal filtrate from the above-mentioned phytosterolin was shaken with a 30% sodium bisulfite solution. The aqueous solution was drawn off, acidified with H_2SO_4 and allowed to stand until the sulfur dioxide had been dissipated. The solution now had an aromatic fragrance. It was extracted with ether. The ether solution showed a residue of an insignificant amount of oil. This was subjected to the color tests characteristic for vanillin. With ferric chloride a green color resulted, similar to the color resulting with dilute vanillin solutions. The phloroglucin and hydrochloric acid test showed a light pink coloration. It is therefore quite probable that this resin contains a trace of vanillin.

A quantity of this resin (277 g.) was dissolved in ether and extracted successively with water, and with solutions of ammonium carbonate, potassium carbonate, and potassium hydroxide. The ether was then washed with water and the solvent removed. This *neutral constituent* weighed 116 g. or 42% of the ether extract. It is an extremely sticky substance and when warmed can be pulled into shiny, silken-like threads. It is very soluble in alcohol. In order to find out whether it was ester like corresponding to the "resinotannolester" group of Tschirch, or a stable substance incapable of hydrolysis ("resene") estimations were carried out upon its saponification value.

1.898 g. boiled 0.5 hr. with 23 cc. 0.5 *N* KOH (alcoholic), neutralized 0.3136 g. KOH. S. V. = 165.

1.898 g. boiled 1.0 hr. neutralized 0.333 g. KOH. S. V. = 175.5.

1.898 g. boiled 5 hrs. neutralized 0.3416 g. KOH. S. V. = 179.

It appeared, therefore, that some insight into the composition of this amorphous resin might be gained by hydrolysis. For this purpose 35.5 g. were dissolved as far as possible in 350 cc. of 10% KOH, and steam

was passed through the mixture for about one week. The liquid when acidified gave an oily precipitate, and the acid filtrate was examined for organic acids with negative results. Saponification with 20% KOH solution for a somewhat longer period gave no smooth reaction, although small quantities of volatile acids were detected as decomposition products.

Another portion (33 g.) was hydrolyzed by the method of Tschirch¹ using at first sulfuric acid 1 : 2. After distilling with steam for 4 days, 0.915 g. of umbelliferon was obtained. The strength of the sulfuric acid was increased to 1 : 1 and after about ten days 3.86 g. further of umbelliferon was obtained. The total umbelliferon corresponds to 14.3% of the neutral portion. It gave the characteristic fluorescence with alkalis, and after recrystallizations from water, dilute alcohol, and ethyl acetate melted at 228°.

Calc. for $C_9H_6O_3$: C = 66.67, H = 3.7. Found: C = 66.86, H = 3.43.

The resin or ester is therefore somewhat similar to some other resins of the umbelliferae such as galbanum, sagapen, asafoetida, which yield umbelliferon when thus hydrolyzed.

The ammonium carbonate extract of the ether extract of the resin was acidified and permitted to stand for some time when a quantity of tar separated. This was removed by filtration and the clear aqueous acid filtrate thoroughly extracted with ether. This solution was evaporated to dryness and dried *in vacuo* over sulfuric acid. When now it was digested with small volumes of anhydrous ether a white crystalline deposit remained, weighing 0.24 g. It was crystallized from water whereupon it melted at 205–206°. It was dried for 2.5 hours at 125° and analyzed. The remainder was again recrystallized from dilute alcohol whereupon it separated in needles and the melting point remained constant. This was dried at 115° and also analyzed.

I. 0.0853 g. subst. gave 0.1802 g. CO_2 and 0.0357 g. H_2O . II. 0.0641 g. subst. gave 0.1351 g. CO_2 and 0.0270 g. H_2O .

Calc. for $C_9H_8O_4$: C = 57.1; H = 4.8. Found: C = 57.61, 57.48; H = 4.69, 4.73.

This acid appears to be vanillic acid (3-methoxy protocatechuic acid). This was further substantiated by the determination of the methoxyl group upon another small sample.

The potassium carbonate extract of the ether extract upon acidification yielded a tar which was removed by filtration. From the filtrate about 0.2 g. of umbelliferon was isolated. Recrystallized from hot water it melted at 226° and when a mixture of this product with the umbelliferon that was obtained from the glucoside by hydrolysis was melted, the melting point was 227°.

Calc. for $C_9H_6O_3$: C = 66.67; H = 3.7. Found: C = 66.9; H = 3.7.

¹ "Die Harze und die Harzbehälter," 1906, p. 342.

When the potassium hydroxide extract was redissolved in alcohol it was impossible to obtain crystalline products even after the solution was stood aside for months. Thus the resinous extract weighed 143 g., equivalent to 52% of the ether extract. It showed no ester properties, and was in fact a resin acid. (Acid no. = 129.) A portion (106 g.) was dissolved in a large volume of ether and again extracted with solutions of ammonium carbonate and of potassium carbonate. The ammonium carbonate solution was acidified and a smear precipitated, indicating that the substances extracted with potassium hydroxide had undergone change. The filtrate from this smear yielded a quantity (0.1 g.) of vanillic acid that melted after recrystallization from water at 204–205°. A methoxyl determination was carried out upon this, by the Zeisel method as modified by Perkin.

Calc. for $C_9H_8O_4 \cdot OCH_3$ = 18.4%. Found: 18.3%.

The potassium carbonate extract contained a small quantity of umbelliferon.

The potassium hydroxide extractions were made with successive portions of 100 cc. of a one per cent. solution. These were each washed once with ether and then acidified with hydrochloric acid and the sumbul resin acid was again extracted with ether. The ether was removed and the residues were dried in a vacuum over sulfuric acid. The first four extracts weighed about 12 g. each and the fifth to the tenth and last extract were smaller. Fourteen grams of material could not be extracted with 1% potassium hydroxide solution. The fractions of this resin acid were examined and found to be mixtures, although they were all similar light-colored powders when dry and of a hygroscopic nature. When very slightly moistened with alcohol they became exceedingly sticky and resinous.

Fraction III. This was a typical product. It softened at 56–60° and became translucent at 63°, and decomposed with effervescence at 75–85°. It was analyzed: C = 72.3%; H = 8.1%. It had an acid number of 118–122, and was optically active.

0.474 g. made up to 50 cc. with 95% alcohol showed a rotation of -1.18° in a 2 dcm. tube, whence $[\alpha]_D^{21.5} = -62.2^\circ$.

Fraction IV. This fraction softened at 50° and was completely translucent at 53°. It effervesced at about 80–90°. Analysis showed: C = 73.3%; H = 8.2%; acid number = 123.

0.3942 g. made up to 20 cc. with 95% alcohol showed a rotation of 2.22° in a 2 dcm. tube, whence $[\alpha]_D^{19.5} = -56.3^\circ$.

Fractions V and VI. The optical rotation was taken.

V. 0.4293 g. made up to 20 cc. with 95% alcohol showed a rotation of 1.98° in a 2 dcm. tube, whence $[\alpha]_D^{20} = -46.0^\circ$.

VI. 0.7665 g. made up to 20 cc. with 95% alcohol showed a rotation of 1.56° in a 1 dcm. tube, whence $[\alpha]_D^{22} = -40.6^\circ$.

It is therefore obvious that this sticky acid of a resinous nature, which forms a most conspicuous part of sumbul extract and gives the latter its disagreeable properties is not a homogenous body. The presence of vanillic acid in the solution after prolonged standing of the alcohol solution suggested that this phenolic acid represents a part of the structure of the complex resin and a methoxyl determination of the resin acid further indicates this.

Subst. 0.1918 g.: $\text{CH}_3\text{I} = 0.0641$. Found: $\text{OCH}_3 = 4.4\%$.

Vanillic acid was prepared from this resin acid as follows: thirteen grams were boiled for several hours with 5% alcoholic sulfuric acid. The alcohol was removed by steam distillation. The steam distillate contained a small amount of a blue oil resembling the essential oil.

The contents of the flask were shaken with ether, which was then extracted with solutions of ammonium carbonate, potassium carbonate, and potassium hydroxide. From the first of these extracts vanillic acid melting at $205-206^\circ$ was isolated. The weight was 0.5 g. The potassium carbonate extract yielded umbelliferon (0.05 g.) melting at $225-227^\circ$. Nothing definite could be isolated from the potassium hydroxide solution.

The chloroform extract of the resin (46 g.) was divided into two parts. The first (26 g.) was redissolved in chloroform and extracted with the various alkaline solutions but nothing definite could be separated by this process. Most of the material was extracted with potassium hydroxide solution. Twenty grams were hydrolyzed with 5% alcoholic sulfuric acid. Umbelliferon (0.85 g.) melting at $226-227^\circ$ was isolated. This was present in glucosidic combination, as 1.5 g. of *d*-phenyl glucosazone melting at $206-207^\circ$ was isolated.

The ethyl acetate extract of the resin (19 g.) was a dark-colored resinous product. Upon hydrolysis a small amount of umbelliferon melting at $226-227^\circ$ was isolated, but sugar was not formed. The material is therefore not glucosidic.

The alcohol extract of the resin (18 g.) agreed in its properties with the brown glucosidic powder isolated from the amyl alcohol extract of the constituents soluble in water. Umbelliferon and a reducing sugar were found as products of an acid hydrolysis.

KALAMAZOO, MICH.

[CONTRIBUTION FROM THE LABORATORY OF THE DODGE AND OLCOTT Co.]

SOME DERIVATIVES OF COUMARIN.¹

By FRANCIS D. DODGE.

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The behavior of unsaturated lactones, or more particularly, the coumarins, with the alkaline bisulfites, appears so far to have been studied in but one instance.

¹ Presented at the meeting at New Orleans, Mar., 1915.