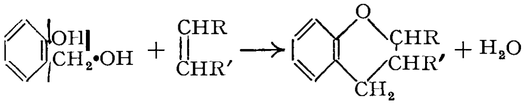
128. *Rubber, Polyisoprenes and Allied Compounds. Part V. The Chemical Linking of Rubber and of Other Olefins with Phenol–Formaldehyde Resins.*

By J. I. CUNNEEN, E. HAROLD FARMER, and H. P. KOCH.

Rubber, isoprenic olefins, and doubtless most olefinic substances combine in virtue of their unsaturation with the condensation products of phenol and formaldehyde to give chroman derivatives. The detailed structure of the combination products, the relation of chroman-formation to the formation of phenol–formaldehyde resins, and the significance of certain ancillary features of the reaction are discussed.

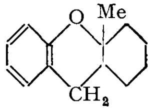
RUBBER combines readily with maleic anhydride (Bacon and Farmer, *Proc. Rubber Tech. Conf.*, 1938, p. 256) up to a limit of one molecule of the latter per isoprene unit of the former. The comparative ease of occurrence of this reaction made it seem feasible to use maleic and similar unsaturated anhydrides (or acids) as a means of linking rubber chemically with various types of hydroxylic compound, the ethylenic carbon pairs of the maleic molecules serving to form C–C links with the rubber, and the anhydro-groupings to form ester links with hydroxy-compounds. Although it was possible to carry out this linking process successfully in a number of examples, the combination of rubber with phenol–formaldehyde resins could be much more satisfactorily effected if the rubber–maleic anhydride compound was not pre-formed, but, instead, a somewhat oxidised rubber together with maleic anhydride, phenol, and formaldehyde were simply heated together until resin formation occurred (Redfarn and Schidrowitz, B.P. 507,995). Subsequently, it was found that considerably oxidised rubber (oxygen, *ca.* 10—13%; *M*, 3000—4000) reacted more readily than slightly oxidised rubber, the product being a thermo-setting resin of Bakelite type, remarkable in possessing valuable residual thermoplastic properties. Investigation of the chemical reaction by which this resin is produced has given rather unexpected results in the field of additive reactions, and has thrown new light on the process of resinification.

It was soon discovered that maleic anhydride could be satisfactorily replaced by oxalic or acetic acid, and no evidence could be gained that any appreciable degree of esterification of the anhydride units by the hydroxylic phenol–formaldehyde components occurred. Hence the maleic anhydride clearly functioned largely as a mild acid catalyst. The great improvement in the ease of condensation which followed the replacement of lightly oxidised by considerably oxidised rubber seemed at first to indicate that a reaction of aldol type took place between the ·CHO or ·COMe end-groups of the shortened rubber chains and the keto-tautomer of phenol, or alternatively that elimination of water occurred between hydroxyl groups in the oxidised rubber and the aromatic nuclei of the phenol. Thorough experimental examination, however, of these possibilities led to their dismissal from further consideration (the experimental details have been omitted). There remained, then, no very reasonable alternative to the conclusion that rubber, and therefore probably most olefinic substances, are able, in virtue of their olefinic unsaturation, to combine with phenol and formaldehyde at some stage in the intercondensation of the latter, and this conclusion was reinforced by certain experiments carried out by Hilditch and Smith in 1935 (*J. Soc. Chem. Ind.*, **54**, **111**) which strongly indicated that drying-oil esters are able because of their unsaturation to combine with a simple *p*-cresol–formaldehyde condensation product. Any remaining doubt as to the capacity of olefinic materials to unite or condense with simple phenol–formaldehyde condensation products was removed by the publication at this point of a paper by Hultzsch (*J. pr. Chem.*, 1941, **158**, 275; *Chem. Abs.*, 1942, **36**, 849), in which the result of heating saligenin with styrene was

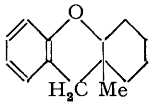


reported to be the formation of 2-phenylchroman, and that of heating several other simple phenol–formaldehyde condensation products containing ·OH and $\cdot CH_2\cdot OH$ groups in *o*-positions with olefinic alcohols, esters, etc., was the formation of analogous chroman derivatives. Curiously enough, however, *cyclo*hexene was reported not to undergo condensation with saligenin.

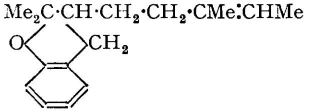
We found on examining the behaviour towards saligenin of the two simple analogues of rubber, 1-methyl*cyclo*hexene and dihydromyrcene, that reaction in each case occurs readily at 180°, giving by loss of water a non-hydroxylic, oxygen-containing condensation product having the general properties and empirical composition to be expected for chroman structures of the type reported by Hultzsch. The di-olefin, dihydromyrcene, however, formed a di- as well as a mono-saligenino-condensation product, the two compounds resembling one another in containing no active hydrogen, but differing in containing respectively no hydrogenisable double bond, and one such bond. For the *compound* from 1-methyl*cyclo*hexene, (I*a*) and (I*b*) are possible formulæ, but since any addition of a reagent to an unsymmetrical olefin $CRR'{:}CH_2$ or $CRR'{:}CHR''$ normally proceeds almost entirely in one direction (as determined by the relative polarity of the ethylenic carbon atoms) (I*b*) is unlikely to represent any considerable proportion of the product unless the addition reaction involves radical forms (see below). Similarly for the two compounds from dihydromyrcene the monosaligenin *compound* is likely to be mainly (II*a*) or (II*b*), and the disaligenin *compound* (III). It was very significant from the point of view of successful resin-formation, however, that the monosaligenin compound from 1-methyl*cyclo*hexene was accompanied by a small amount of a disaligenin *compound*, $C_{21}H_{24}O_2$. This contained one atom of active hydrogen per molecule and apparently represented the simplest possible example of the linking of a polycondensed phenol–formaldehyde chain (*i.e.*, a Novolak) to the olefin.* This compound is formulated in (IV), the point of attachment of the hydroxybenzyl group to the aromatic nucleus of the chroman unit being presumably *o*- or *p*- to the chroman oxygen.



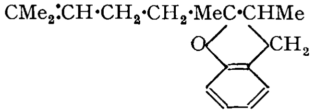
(I*a*.)



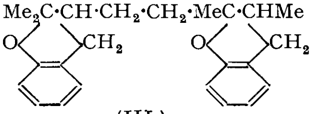
(I*b*.)



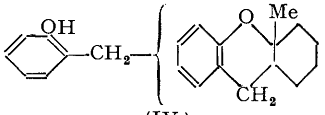
(II*a*.)



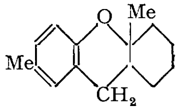
(II*b*.)



(III.)



(IV.)



(V.)

When purified rubber (1 mol.) in benzene was heated with saligenin in two different proportions (0·18 and 0·27 mol.) two distinct oxygenated products were formed. These proved to contain hydroxylic (presumably phenolic) as well as ethereal oxygen, in the ratios 1 : 2 and 5 : 8, so indicating that most of the oxygen was present in simple chroman units such as those in (III), and that roughly one chroman unit per 14 or per 8 isoprene units of the rubber was present. Not more than 1 in 2 or 5 in 8 (respectively) of the chroman units could thus be carrying a hydroxybenzyl substituent, or, if still larger phenol–formaldehyde substituents than hydroxybenzyl were present, then the proportion of chroman units carrying side chains (of any kind) would be smaller still. Confirmation of the constitutions advanced above has been sought by spectrographic means.

Absorption Spectra.—Webb and others (*J. Org. Chem.*, 1939, **4**, 389) gave data for the light-absorption in hexane solution of a number of alkyl-substituted phenols, chromans, and coumarans, all of which exhibit a group of two or more narrow bands in the region 2700—2900 A. They found that the formation of chroman or coumaran rings by cyclisation of *o*-alkylphenols is regularly associated with a well-marked increase and

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* No long Novolak chains were to be expected, since an excess of olefin was always used

bathochromic shift of absorption, and that the exact location and intensity interrelationships of the fine structure bands is also highly characteristic of any given compound. We have therefore determined the ultra-violet absorption spectra (in *cyclo*hexane solution) of saligenin and its various condensation products for purposes of identification.

Saligenin itself (Fig. 1, curve *a*) gives rise to two bands near 2730 and 2800 A., closely similar to the spectra of *o*-cresol (Hogness, Sidwell, and Zscheile, *J. Biol. Chem.*, 1937, **120**, 251) and *o*-allylphenol (Webb *et al.*, *loc. cit.*) which only differ in the nature of the *o*-alkyl substituent. This absorption is intensified and displaced towards longer wave-lengths on passing to the compound of saligenin with methyl*cyclo*hexene (I*a*) (cf. Fig. 1, curve *b*), which is characterised by two steep maxima situated at precisely the same wave-lengths as the two bands of 2 : 2-dimethylchroman measured by Webb *et al.* (2775 and 2845 A.; minimum at 2815 A.). The width and relative height of the bands are also the same for both compounds, although all our intensities are consistently higher than Webb's on the absolute molecular scale ($\varepsilon = 3100$ at 2845 A.). The new compound evidently contains the same chromophoric grouping as 2 : 2-dimethylchroman, and its formulation as a methyl-substituted hexahydroxanthen (I*a*) may be considered as established beyond any doubt.

FIG. 1.

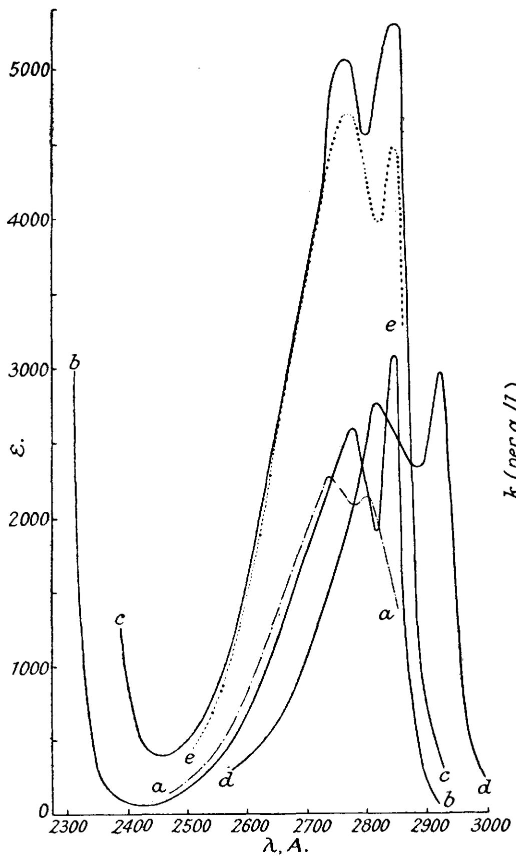
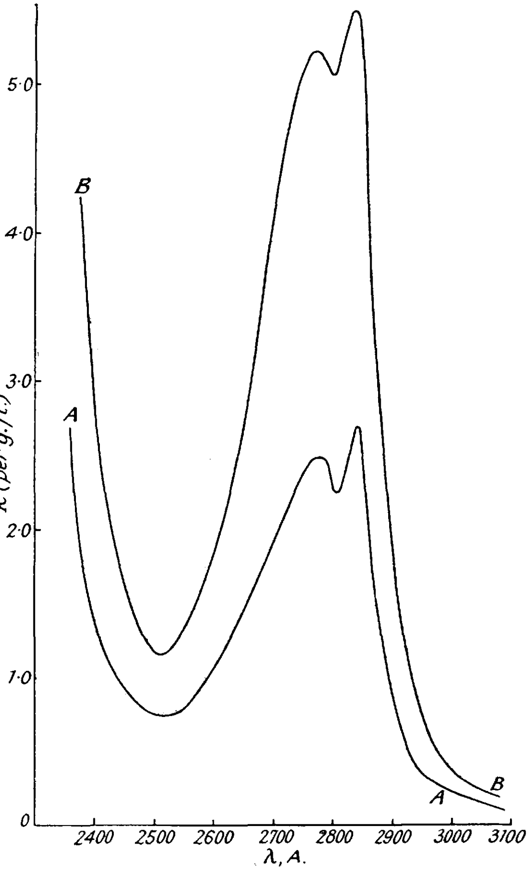


FIG. 2.

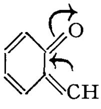


Again, the two substances $C_{17}H_{24}O$ and $C_{24}H_{30}O$ obtained by condensation of saligenin with dihydromyrcene, at one and at both (respectively) of the double bonds of the latter, exhibit absorption curves identical with the above. The molecular extinction coefficients at 2845 A. are now 3000 and 5650 respectively, in good agreement with the proposed structures (II, *a* or *b*) and (III) which contain the 2 : 2-dialkylated chroman chromophore once or twice in the dihydromyrcene chain. Although the spectra of (II*a*) and (II*b*) would be indistinguishable, it seems likely that all our chroman derivatives must carry the extra methyl groups derived from the olefin in the 2-, and not the 3-position in order to produce complete identity with the spectrum of Webb's prototype.

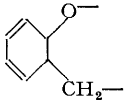
Curve *c* of Fig. 1 shows the extinction values of the solid hydroxybenzyl-substituted chroman derivative (IV). Its total absorption must be expected to bear close resemblance to the sum of the separate absorptions contributed by the *o*-hydroxybenzyl and the (nuclear-substituted) chroman chromophores which are effectively isolated from one another in the compound molecule (cf. Jones, *Chem. Rev.*, 1943, **32**, 2). This sum is graphically represented by the dotted curve *e*, except in the important respect that no allowance is made for the effect of nuclear substitution on the spectrum of the chroman system shown in curve *b*. We have been able to test that effect directly as regards the *p*-position by synthesising the *p*-methyl *derivative* (V) (curve *d*). The general appearance of the spectrum remains unchanged, but a significant displacement of the maxima to 2815 and 2920 A. is observed. Since it is known that such bathochromic shifts are largely independent of the precise nature of the alkyl substituent (methyl, ethyl, and benzyl groups all displace the absorption of benzene to longer wave-lengths; cf. Ley and Dirking, *Ber.*, 1934, **67**, 1333), it must be concluded that the hydroxybenzyl derivative (IV), in giving rise to a spectrum that terminates very abruptly beyond 2845 A., cannot contain the substituent affixed in the *p*-position. On the other hand, the difference between the observed and the constructed curve, *c* and *e*, can be well accounted for by formulating the hydroxybenzylchroman with the hydroxybenzyl group attached at the *o*-carbon atom. Both phenol and *o*-cresol (but not *p*-cresol) exhibit maximum absorption at the same wave-lengths (Wolf and Herold, *Z. physikal. Chem.*, 1931, *B*, **13**, 229), and the near-ultra-violet band of 2-methylcoumaran is considerably intensified but not displaced as the result of *omm'*-trisubstitution (Webb *et al.*, *loc. cit.*). It has, indeed, been stated as a general rule for aromatic compounds that *o*-substitution produces only slight, and *p*-substitution relatively marked, bathochromic effects (Morton and Stubbs, J., 1940, 1347).

Finally, the absorption spectra of the two rubber–saligenin compounds (containing 2·25% and 4·15% of total oxygen respectively) were measured in solutions of *cyclo*hexane containing 10% of ethyl alcohol. This choice of solvent was governed by the difficulty of obtaining optically clear solutions, but it was found that none of the curves of Fig. 1 was appreciably altered by addition of the alcohol. Purified rubber itself does not exhibit selective absorption in the quartz ultra-violet, and the typical steep maxima at 2845 and near 2775 A. of the curves *A* and *B* (Fig. 2) obtained for the two rubber derivatives must clearly be attributed to the presence of the chroman chromophore attached to the rubber chain. Allowance being made for increased general absorption, and a 5 : 8 ratio of phenolic to ethereal oxygen (see above) being assumed, the maximum specific extinction coefficient of curve *B* indicates that an average number of one in every ten isoprene units has reacted with a saligenin or *o*-substituted saligenin group. This figure is rather lower than the value of one in eight obtained from the total oxygen content, but certainly serves to show that the bulk of the saligenin must be attached to the rubber molecule by way of the chroman linkage.

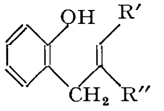
Mechanism and Course of Reaction.—The precise mechanism by which the reactive groups of saligenin or other *o*-hydroxybenzyl alcohols unite with olefinic centres is not easy to determine. It might be supposed that the phenolic alcohol loses water internally to give momentarily either a strongly polarised form (*a*) or a resonating radical form (*b*), or else condenses directly with the olefin to give (*c*) as intermediate. The last course is not a likely one for non-benzenoid primary alcohols to pursue, and the lability of the hydroxyl group must arise from the nearness of the phenolic nucleus. This being so, probably the keto-form (*d*) of the phenolic alcohol is responsible for the reaction, undergoing internal dehydration to give the vinyl ketone (*a*). If combination of this ketone with the olefin occurred in Diels–Alder fashion (cf. the dimerisation of methyl vinyl ketone, Alder *et al.*, *Ber.*, 1941, **74**, 905, 926) to some extent through the form (*b*) and not wholly ionically through (*a*), the final condensation products would be likely to contain many isomeric forms (*e.g.*, I*b* as well as I*a*). The spectrographic evidence, however, does not point to the existence of the additional forms which would arise by *two*-direction addition of olefin to ketone.



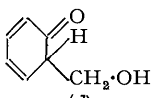
(*a*)



(*b*)



(*c*)



(*d*)

As regards the conclusion that attachment of the hydroxybenzyl side chain in (IV) is restricted to the *o*-position in the chroman system (and this appears to apply also to the points of junction of the side chains in the rubber derivatives), it should be pointed out that the restriction may well not hold between phenol–formaldehyde units *throughout* the longer Novolak chains which would normally be formed where higher proportions of phenol and formaldehyde to olefin and an acid condensing catalyst were used. Also, it is quite likely that when maleic anhydride is used as the acid catalyst some or all of it ultimately combines with the phenol–formaldehyde condensation products, since Hultzsch found that ethyl maleate combines readily with these. The superior ease of combination of highly oxidised rubber over rubber hydrocarbon appears to be solely a function of miscibility of the reactants. The greatly shortened, oxygenated chains of the highly oxidised rubber (*M*, 3000—4000) dissolve fairly readily in boiling phenol, whereas rubber is insoluble.

The rubber-linked Novolaks formed in presence of an acid catalyst are capable of being cross-linked to yield three-dimensional molecular networks of the Bakelite type when heated in the ordinary way with hexamethylenetetramine. The resulting thermosetting products, however, soften when they are heated to 120—130° and harden again when they are cooled.

EXPERIMENTAL.

1-*Methyl*cyclo*hexene.*—The hydrocarbon, b. p. 110°, was obtained by dehydration of 1-methyl*cyclo*hexanol in the presence of a little iodine (Found : C, 87·45; H, 12·65; I.V., 265. Calc. for C_7H_{12} : C, 87·5; H, 12·5%; I.V., 265).

o-*Hydroxybenzyl Alcohol.*—Commercial saligenin, crystallised twice from ethyl alcohol–benzene (15 : 85 by vol.) formed colourless plates, m. p. 86° (Found : C, 67·85; H, 6·5. Calc. for $C_7H_8O_2$: C, 67·7; H 6·44%).

12-*Methyl*-1 : 2 : 3 : 4 : 12 : 13-*hexahydroxanthen* (I*a*).—Saligenin (40 g.) was heated with excess of 1-methyl*cyclo*-

hexene (200 c.c.) for 4 hours at 180° in sealed tubes. The tubes, on cooling, contained a pale yellow solution and a little water; the latter was removed with anhydrous copper sulphate. After the excess of olefin had been removed by distillation at reduced pressure a syrup (54 g.) remained. This syrup was dissolved in benzene (500 c.c.), washed twenty times with aqueous 2N-caustic potash (4 l.), and finally with water until neutral. The benzene solution was dried, and the solvent removed by distillation, leaving a pale yellow, mobile oil (43 g.). Fractional distillation of this oil, through a Fenske column, furnished 12-*methyl*-1 : 2 : 3 : 4 : 12 : 13-*hexahydroxanthen* (30 g.), a colourless, non-solidifying, mobile oil, b. p. 138—139°/10 mm. (Found : C, 83·15; H, 9·0. $C_{14}H_{18}O$ requires C, 83·17; H, 8·9%). A brown thermoplastic residue (13·0 g.) remained.

The oily condensation product did not possess ketonic or aldehydic properties and was not hydrolysable. A sample of it did not absorb hydrogen when shaken for 6 hours with the gas in presence of Adams's catalyst; a similar sample failed to liberate methane when treated with methylmagnesium iodide according to Bolland's modification of the Zerewitinov method. The condensation product, therefore, was an ether, without non-benzenoid unsaturation or hydroxyl groups.

5-o-*Hydroxybenzyl*-12-*methyl*-1 : 2 : 3 : 4 : 12 : 13-*hexahydroxanthen* (IV).—The undistillable thermoplastic residue (2 g.) was purified by dissolving it in benzene–petroleum (1 : 1 by vol.; 300 c.c.), running the solution through a column of alumina, and well washing the adsorbate with the same solvent (2 l.). The filtrate gave on evaporation the *compound* (IV) (1·2 g.), in which the *o*-hydroxybenzyl group, as shown by spectrographic examination, occupied the 5-position. This was an amorphous resinous solid (Found : C, 81·8; H, 8·0; OH, 5·3. $C_{21}H_{24}O_2$ require C, 81·8; H, 7·8; OH, 5·5%).

Dihydromyrcene.—Myrcene, prepared from bay oil (*Pimenta acris*) by the method of Power and Kleber (*Pharm. Rundschau*, 1895, **13**, 60), was reduced with sodium and alcohol as described by Semmler and Mayer (*Ber.*, 1911, **44**, 2010). The hydrocarbon, after being twice distilled over sodium through a Fenske column, boiled at 58—59°/16 mm. (Found : C, 87·05; H, 13·0; I.V., 364. Calc. for $C_{10}H_{18}$: C, 86·9; H, 13·1%; I.V., 368).

Monosaligenino-dihydromyrcene.—Saligenin (24 g.) was heated with dihydromyrcene (120 c.c.) for 2 hours at 180° in a sealed tube. The condensate was isolated in the usual manner and the yellow oil (32·6 g.) so obtained was fractionally distilled. *Monosaligenino-dihydromyrcene* (20·2 g.), b. p. 118°/0·05 mm., probably consisting mainly of 2 : 2-*dimethyl*-3-(γ-*methyl*-Δ^{γ}-*pentenyl*)*chroman* (II*a*), was first obtained (Found : C, 83·4; H, 9·9. $C_{17}H_{24}O$ requires C, 83·5; H, 9·85%). Further distillation gave nearly pure *disaligenino-dihydromyrcene* (5·4 g.), a viscous brown syrup, b. p. 200—205°/0·05 mm. Purification of the latter by adsorbing it on alumina from solution in petroleum, followed by elution of the adsorbate with benzene–petroleum (1 : 1 by vol.), gave an almost colourless syrup, doubtless α-(2 : 2-*dimethylchromanyl*-3)-β-(2 : 3-*dimethylchromanyl*-2)-*ethane* (III) (Found : C, 82·3; H, 8·7. $C_{24}H_{30}O$ requires C, 82·3; H, 8·6%). The monosaligenino-compound (0·2659 g.), in ethanol solution, absorbed hydrogen (24·8 c.c. at N.T.P.) equivalent to one double bond per molecule when shaken for 6 hours with Adams's catalyst (0·1 g.). The disaligenino-compound under the same conditions did not absorb hydrogen. Neither derivative gave any methane with methylmagnesium iodide under Bolland's modified conditions of Zerewitinov hydroxyl determination, and neither showed ketonic or aldehydic properties or was hydrolysable.

Rubber.—For convenience, a " sol " fraction of rubber, obtained by partial dissolution of crepe rubber in light petroleum (b. p. 40—60°), was employed. The crepe rubber was cut up and thoroughly extracted with acetone in the usual manner, and the residue then extracted with light petroleum in the all-glass modification of Pummerer, Andriessen, and Gündel's apparatus described by Bloomfield and Farmer (*Trans. Inst. Rubber Ind.*, 1940, **16**, 69). In the latter operation the extracts obtained in the first 48 hours were rejected as containing oxygenated rubber, and the later extracts were well mixed and their rubber content precipitated by addition of excess of 95% alcohol. The solvent and alcohol adhering to the rubber were removed by evaporation at 10 mm. pressure, and the rubber finally dried for 48 hours at room temperature and 10^{-5} mm. pressure. The rubber so obtained was kept under a high vacuum in the dark (Found : C, 88·05; H, 11·95; I.V., 371; *M*, 361,000. Calc. for C_5H_8 : C, 88·2; H, 11·8%; I.V., 372).

Saligenino-rubber.—Rubber (1·0 g.) was dissolved in toluene (25 c.c.) and heated with saligenin (0·33 g.) in a sealed tube containing oxygen-free nitrogen for 4 hours at 180°. After cooling, the tube contained a pale yellow solution and some water. Benzene (150 c.c.) was added, and the solution dried over anhydrous sodium sulphate, filtered, and concentrated under nitrogen at reduced pressure to 35 c.c. The clear solution so obtained was poured into an excess of ethyl alcohol, which precipitated the saligenino-rubber as a white rubber-like solid, leaving the self-condensation products of saligenin in solution. The precipitate was washed once with ethyl alcohol and thoroughly dried for 48 hours at 10^{-5} mm. by distillation of all solvent into a liquid-air trap (Found : C, 86·5; H, 11·25; OH, 0·8%; *M*, 119,000). Assuming that all the non-hydroxylic oxygen is ethereal, we calculated that one chroman linkage was present per 14 isoprene units (cf. the value found spectroscopically). A second saligenino-rubber, a white rubber-like solid, was prepared by heating rubber (1·8 g.) in toluene with a larger proportion of saligenin (0·9 g.) than was used in the foregoing experiment (Found : C, 85·3; H, 10·55; OH, 1·8%; *M*, 69,000). In this derivative one chroman linkage was present per eight isoprene units as calculated from the above analytical data.

7 : 12-*Dimethyl*-1 : 2 : 3 : 4 : 12 : 13-*hexahydroxanthen* (V).—2-Hydroxy-5-methylbenzyl alcohol, m. p. 105° (3 g.), was heated with 1-methyl*cyclo*hexene (15 c.c.) for 3 hours at 180° in a sealed tube. The pale yellow liquid product was freed from water by drying over anhydrous sodium sulphate, and then from solvent. The syrupy residue (3·8 g.) was dissolved in " AnalaR " benzene, and the solution washed twenty times with 2N-aqueous potassium hydroxide. The solvent was then removed, and the residue (3·3 g.) fractionally distilled. The first fraction had b. p. 147—150°/10 mm. (Found : C, 82·95; H, 9·4. $C_{15}H_{20}O$ requires C, 83·25; H, 9·3%), and the non-homogeneous residue consisted of substances of somewhat higher oxygen content.

Spectrographic Measurements.—The spectra were recorded on Kodak B-10 plates, using a Spekker Photometer and Hilger Small Spectrograph, which gives a dispersion of 35 A./mm. in the region of 2800 A. *cyclo*Hexane and ethyl alcohol were both purified for spectroscopic use.

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