though a chlorine solution is used which is three times the maximum concentration considered safe by Chattaway and Orton.[6] The method is rapid and the product is better than 99.7% pure.

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Note on Caryophyllin and Urson.—In a previous article[1] the writer reported the results of an examination of caryophyllin and urson, two very similar and probably isomeric compounds, having apparently the composition $C_{30}H_{48}O_3$ and exhibiting properties which could best be explained by the assumption of an oxy-lactone structure, or the grouping $\left\{\begin{array}{l}\text{—OH}\\ \text{—O—}\\ \text{—CO}\end{array}\right.$

More recently urson has been studied by van der Haar,[2] who has arrived at the conclusion that the alternative formula, $\left\{\begin{array}{l}\text{—OH}\\ \text{—COOH}\end{array}\right.$, which is that of an hydroxy acid, has been demonstrated. The arguments against this formula have already been noted by the writer. Van der Haar also criticizes the methods employed by the writer as "uncontrolirbar" in comparison with elementary analyses, but in reality, the titrations used to show the functional relations of these compounds can be "controlled" or checked with the utmost ease, and they were employed exactly because they are more conclusive and satisfactory for the purpose in view than combustions.

It was found that caryophyllin and urson could be titrated with accuracy in alcoholic solution, the results indicating one carboxyl or lactone group in the C_{30} molecule. On acetylation, two acetates were obtained; one, an unstable diacetate, convertible by boiling with alcohol into a stable mono-acetate, which in turn yielded the original caryophyllin or urson by hydrolysis with alkali. These results appeared to be explainable only by the oxy-lactone formula. Van der Haar, however, obtained from urson an acetate, melting at 200°, which on boiling with alcohol gave a compound melting at 275°, which without further examination he assumed to be urson. Inasmuch as urson melts at about 285° and the mono-acetate at about 265°, the identification is rather unsatisfactory. In view of the importance of this fact for his hypothesis, a more thorough examination of the product would have been desirable. A quantitative hydrolysis would have been conclusive. In two later articles[3] van der Haar has revised his previous

[6] Chattaway and Orton, *J. Chem. Soc.*, **75**, 1046 (1899).

[1] Dodge, THIS JOURNAL, **40**, 1917 (1918).

[2] Van der Haar, *Rec. trav. chim.*, **43**, 367, 542 (1924).

[3] Van der Haar, *ibid.*, **46**, 775 (1927); **47**, 585 (1928).

conclusions and, employing the methods used by the writer finds, in fact, that caryophyllin (which is shown to be identical with the sapogenin of beets, and also with the oleanol of Power and Tutin)[4] yields two acetates. Urson also gave two similar derivatives.

To reconcile these facts with the hydroxy acid formula, which permits but one acetyl derivative, he suggests for the compound described by the writer as diacetate, the formula $[C_{30}H_{48}(OAc)CO]_2OAc_2O$, which represents the anhydride of the acetylated hydroxy acid combined with one molecule of acetic anhydride "of crystallization!" On treatment with alcohol this is supposed to yield the monoacetate, $C_{30}H_{48}(OAc)COOH$.

It is hardly necessary to point out the anomalous nature of this hypothesis. If the first compound is really a molecular compound of an acid anhydride with acetic anhydride, boiling with alcohol should, by all analogy, yield an ester, and not the free acid. To the writer, the lactone formula appears less involved in difficulties.

Van der Haar also claims to have "proved," from the results of two combustions, the formula of urson to be $C_{31}H_{50}O_3$, instead of the previously accepted $C_{30}H_{48}O_3$. How much importance should be ascribed to this is not clear. Equally good analyses may be cited for the latter formula. It is to be noted, however, that Power and Tutin found the composition $C_{31}H_{50}O_3$ for oleanol (probably identical with caryophyllin) and prunol (apparently identical with urson), thus agreeing with van der Haar. The former also described two acetates of oleanol, and considered it to be a phenol. Yet this assumption, as well as the hydroxy acid hypothesis, seems to be contradicted by the insolubility of these compounds in aqueous alkali. Furthermore, both compounds show an unusual stability at high temperatures. They may be sublimed without decomposition: caryophyllin, in fact, is slowly volatile in steam, and has been frequently observed by the writer as an almost pure sublimate on the covers of stills used for the extraction of oil of cloves. This stability seems to the writer to indicate very definitely the lactone structure. Compare, for example, *o*-coumaric acid, a typical hydroxy acid, which decomposes at its melting point, and its lactone, coumarin, which distils without decomposition at 280°.

To sum up, the question as to the elementary composition of these compounds may be considered as open, with the evidence rather in favor of the C_{30} formula. As to the functions of the oxygen atoms, the writer is still of the belief that the lactone formula is the only one available.

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[4] Power and Tutin, *J. Chem. Soc.*, **93**, 891 (1908).