REGIO- AND STEREOSELECTIVE GLYCOSYLATION OF 20(S), 24(R)-EPoxydammarane-3, 12β, 25-
TRIOLS WITH CHOLESTERYL (α-D-GLUCOSE ORTHOACETATE). III.

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The glycosylation of 20(S), 24(R)-epoxydammarane-3, 12β, 25-triols under the conditions of the
previous formation of an ion pair with a Lewis acid and subsequent treatment with cholesteryl
(α-D-glucose orthoacetate) leads to the selective formation with high yields of the corresponding
12-monoglucosides having the trans configuration of the glucosidic bond. The regioselectivity
of the direct glycosylation of 20(S), 24(R)-epoxydammarane-3, 12β, 25-triols by orthoesters
is determined by the influence of intramolecular hydrogen bonds in the initial triols. De-
tails of the PMR and 13C NMR spectra of the new compounds obtained are given.

The development of methods for both the selective and the exhaustive glycosylation of tetracyclic dam-
marane polyols of type (I) related to the panaxgenins (Scheme 1) opens up possibilities for obtaining various
analogues of ginseng glycosides [1]. We have previously studied the glycosylation of the title alcohols by the
orthoester method via the intermediate formation of orthoesters and their subsequent isomerization into the
desired glycosides [2].

The isomerization of the 3-monoorthoesters obtained from (I) and (II) led to the anomalous selective
formation of the 12-monoglucosides (III) and (V), in view of which the hypothesis was expressed that the isom-
erization studied takes place in actual fact as the direct intermolecular glycosylation of one molecule of a
3-monoorthoester by another. To confirm this hypothesis, we have investigated the direct glycosylation of
tetracyclic dammarane polyols with a number of orthoesters. The nature of the direct glycosylation of the
triols (I) and (II) with the orthoesters (XII) and (XIII) depends on the nature of the glycosylating agent and
also, to an even greater degree, on the experimental conditions of glycosylation, which is probably connected
with the presence of a strong intramolecular hydrogen bond (intra-HB) between the proton of the 12β-OH
group and the oxygen atom of the tetrahydrofuran (THF) ring in each of the triols (I) and (II).

In the IR spectra of (I) and (II) in CHCl₃ solution (c 37.0 and 34.0 mg/ml, respectively), broad bands of
hydroxyl absorption are observed at 3392 and 3401 cm⁻¹, respectively, which did not change their position and
intensity when the solutions were diluted 25-fold. In the 1H NMR spectra (CDCl₃) of (I) and (II) broad signals
of unit intensity are observed at 5.62 and 5.59 ppm, respectively, which are sensitive to the temperature con-
ditions of recording the spectra and to deuterium exchange. The intra-HBs mentioned may promote the forma-
tion of a bipolar ion of type (XIV) or (XV) on the interaction of (I) or (II) with HgBr₂ (scheme 2).
The glycosylation of (I) and (II) under the conditions of the previous formation of the bipolar ion (XIV) or (XV) followed by treatment with cholesteryl (α-D-glucose orthoacetate) (XII) (experiments 1 and 2) led to the regio- and stereoselective formation of the known 12-monoglucosides (III) and (V) [2] (55 and 53% of theoretical, respectively, calculated on the triols (I) and (II) taken, at a conversion of 60%).

It is interesting to note that the bulk of the cholesterol present in the orthoester (XII) separates out from the solution of the reactants in CH₃NO₂ as the reaction proceeds, thereby promoting an increase in the yield of the glycosides (III) and (V) and the avoidance of side glycosylation reactions.

The glycosylation of (I) under the same conditions with α-D-glucose (t-Bu orthoacetate) (XIII) (experiment 3) led to the formation of a mixture of the 12-monoglucoside (III) (22%), the known 12,25-diglucoside (IV) [2] (9%) and 1"E"-12β-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyl)-3α-hydroxydammar-20(22)-en-24-one (VII) (26%).

At the same time, when the triol (I), the orthoester (XII), and HgBr₂ were mixed simultaneously (experiment 4), there was the formation only of a mixture of 1"Z"-12β-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyl)-3α-hydroxydammar-20(22)-en-24-one (VI) (27%), and 20R,24(R)-epoxydammarane-3α,12β,25-triol (VII) (16%) — the epimer of the initial triol (I) at C²₀.

Doublet signals of the anomeric protons of the sugar component at C¹² in the ¹H NMR spectra of (VI) and